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To cite this article: Lin Tian, Goodarz Ahmadi & Jiyuan Tu (2017) Mobility of nanofiber, nanorod, and straight-chain nanoparticles in gases, *Aerosol Science and Technology*, 51:5, 587-601, DOI: [10.1080/02786826.2017.1280596](https://doi.org/10.1080/02786826.2017.1280596)

To link to this article: <https://doi.org/10.1080/02786826.2017.1280596>



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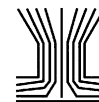
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Mobility of nanofiber, nanorod, and straight-chain nanoparticles in gases

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ABSTRACT

With the fast development of nanotechnology, accurate measurement and classification of nanoparticles are in great need. Nanoparticles frequently appear in non-spherical forms such as long aspect ratio nanofibers, nanotubes, and irregular nano-agglomerates. While the well-developed classical studies were mainly in continuum regime with spherical particles, dynamics of the non-spherical nanoparticles is not fully understood. In this study, orientation-averaged mobility of nanofiber and nanorod (with no preferred alignment) is examined by the methods of Brownian diffusion theory, a combination of collision limited reaction rate theory and the bipolar diffusion charging analysis. Comparisons to empirical predictions from the experimental measurements are also made. The study leads to the discovery of a surface-dominated mobility for high aspect ratio nanoparticles with characteristic Knudsen number greater than 5. In view of the extreme relative length scales between particle size and the gas mean free path, particles of all morphologies can be viewed as point collisions; therefore, the equivalent surface mobility diameter is reasonably justified. This finding has been verified in the current study with high aspect ratio particles. For non-spherical particles of more general forms, further investigation is needed. As expected, accuracy of this approximation reduces as the characteristic Knudsen number decreases. When $Kn(d_p) < 0.1$, the study shows that particle morphology starts to play an important role. A review of particle mobility for all Knudsen number flows is also provided.

ARTICLE HISTORY

Received 1 August 2016
Accepted 3 January 2017

EDITOR

Yannis Drossinos

Introduction

Nanotechnology is fast growing as nano-scale materials exhibit unique properties leading to significantly improved performance. Applications can be found in medical treatment, drug delivery, image processing, chemical catalysis, and new products utilizing nanofibers and carbon nanotubes; therefore, accurate characterization of nanoparticles is of great importance.

Dynamics of spherical particles have been extensively studied, and well-developed theories are available for analyzing particle motion for the entire Knudsen range. In creeping flows, Stokes law expresses the viscous drag acting on a sphere in the continuum regime, while in the free molecular regime, particle dynamics are governed by the gas kinetic theory where particle resistance was given by Epstein (1923) as a consequence of momentum transfer between particle-molecule collisions. Conveniently, the transition regime particle drag can be expressed as a combination of the two with a smooth

transition from collision resistance to continuum viscous friction across the entire flow regimes. Transition theory via a Knudsen number correction to the Stokes drag was developed by Cunningham (1910) and Millikan (1923), and widely used. Meanwhile, from diffusion point of view, Einstein (1905) studied the Brownian motion of small particles and related the diffusion coefficient to particle diameter, gas viscosity, and the temperature.

While the complete description of particle dynamics for a sphere is available (in all flow regimes), such understanding is not fully available for non-spherical particles. Theoretical expressions of the Stokes drag are limited to a few regular-shaped particles such as ellipsoids, cylinders, circular disks, and straight chain of agglomerated spheres (Oberbeck 1876; Jeffery 1922; Oseen 1927; Burgers 1938; Brenner 1963; Batchelor 1970). For irregular-shaped particles, the Stokes drags were mainly investigated experimentally. Fitted dynamic shape factors for the equivalent aerodynamic spheres were frequently

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formulated with measurement in sedimentation tanks. Examples of such studies include McNown and Malaika (1950), Horvath (1974), Lasso and Weidman (1986), Cheng et al. (1988), Haider and Levenspiel (1989), Chhabra et al. (1995), Cichocki and Hinsen (1995), and Tran-Cong et al. (2004). The presence of the rotational torque, acting on the anisometric non-spherical objects, implies the presence of an orientation-dependent Stokes drag. There have been very few studies on non-spherical particle dynamics in free molecular regime. Accurate characterization of these particles faces two challenges: (1) the extreme small-scale approaching high Knudsen number regimes; and (2) the non-spherical morphology. Brenner (1967) derived the general theory of the coupling between the translational and rotational Brownian motions of arbitrary-shaped rigid particles. Gallily and Cohen (1976) studied the dynamic interaction between the Brownian translation and rotation of non-spherical particles. Extending the work of Epstein (1923), Dahneke (1973a) derived the free molecular resistance for disks, cylinders, spheroids, and cubes of positive curvatures. Zhang et al. (2012) numerically simulated the scalar friction factor for an arbitrarily shaped particle by using an orientation-averaged projected area approximation and Monte Carlo method in the free molecular regime. In analogy to that of the spheres, modeling transition regime of non-spherical particle resistance predominantly followed the Cunningham (1910) approach by establishing a smooth transition from the free molecular to the continuum regimes. Such examples include the work of Dahneke (1973b), Asgharian et al. (1988), Cheng (1991), Fan and Ahmadi (2000), Zhang et al. (2012), Tian and Ahmadi (2016a,b), Tian et al. (2016), and Gopalakrishnan et al. (2015a). It should be noted that, due to the ambiguity of equivalent mobility definition, the non-spherical slip correction has appeared in a number of forms.

Experimental measurements of non-spherical particle resistance in free molecular and transition regimes were scarce. Of the very few reported studies, Gentry et al. (1991) measured the diffusion coefficients of chrysotile fibers by relating the fractional penetration and size distribution of the test fibers before and after a diffusion battery. Cheng et al. (1988) measured the drag force and slip correction of aggregated aerosols in a Millikan apparatus. Gopalakrishnan et al. (2015a) investigated the mobility of modest-to-high aspect ratio particles in the transitional and free molecular regimes using a differential mobility analyzer (DMA). Meanwhile, significant researches were devoted to the development of classification instrumentation for nanoparticles of non-specified shapes. Whitby and Clark (1966) and Knutson and Whitby (1975) developed the electrical differential

mobility analyzer (DMA) for submicron particles. Alonso and Kousaka (1996) investigated the mobility shift in the differential mobility analyzer (DMA) due to Brownian diffusion and space charge effects. Thomas (1955) and Boulaud and Diouri (1988) examined the diffusion battery method for aerosol particle size determination in the diffusion regime. Jayne et al. (2000) described the development of an aerosol mass spectrometer (AMS) for submicron aerosol using an aerodynamic aerosol inlet with particle time-of-flight measurement. Wang et al. (2005) provided guidelines of designing the aerodynamic focusing for aerodynamic lenses of nanoparticles. Stolzenburg and McMurry (2008) described the basic equations governing the responses of single and tandem DMA systems and proposed an improved log-normal approximation to the DMA transfer function. Though not a direct measurement of dynamics shape factors, design, and accurate interpretation of the test results are highly related to the understanding of diffusion and electrical mobility of non-spherical particles in these devices.

From non-spherical Cunningham correction to particle instrumentation, equivalent mobility diameter is critical for accurate classification of submicron particles in the free molecular and transition regimes. While Cheng (1991) and DeCarlo et al. (2004) gave systematic reviews of the various components in determining the equivalent diameters, they were not focused on the specific challenges faced by high Knudsen number flows. An appropriate definition of equivalent mobility diameter for submicron particles remains an open question due to the lack of an explicit theory and experimental verifications. Recently, Gopalakrishnan et al. (2015a) was able to measure the electrical mobilities and scalar friction factors of modest-to-high aspect ratio particles in free molecular and transition regimes. Their results were well supported by simulations using a combination of collision limited reaction rate theory and bipolar diffusion charging analysis. Recently, Tian et al. (2016) investigated the diffusion of fibers in a quiescent air and developed a diffusion-equivalent sphere diameter for characterizing fiber mobility driven by Brownian motion. A comparison of the predicted diffusion-equivalent spheres to the measured mobility equivalent diameters for a series of nanorods (Gopalakrishnan et al. 2015b) showed excellent agreement (Tian et al. 2016). Melas et al. (2014, 2015) investigated the friction coefficient and mobility radius of the fractal-like aggregates in the transition regime, and the application to straight chain agglomerates. These studies provided an opportunity to re-examine the high aspect ratio non-spherical particle dynamics, and the development of a convenient equivalent mobility diameter in high Knudsen number flows.

In this study, a review of the equivalent sphere diameter for different applications is given. Then the orientation-averaged mobility of nanofiber and nanorod (with no preferred alignment) is examined by methods of Brownian diffusion theory, a combination of collision limited reaction rate theory, and the bipolar diffusion charging analysis. Comparisons to the empirical predictions from experimental measurements are made. Comparisons of the various mobility diameters suggested the suitability of a surface-dominated mobility for nanoparticles with characteristic Knudsen number greater than 5. In view of the extreme relative length scales between particle size and the gas mean free path, particles of all morphologies can be viewed as point collisions, and therefore, the equivalent surface mobility diameter is reasonably justified. As expected, accuracy of the surface equivalent mobility approximation reduces as the characteristic Knudsen number decreases. When $Kn(d_L) < 0.1$, the study shows that particle morphology starts to play an important role. Using the diffusion equivalent diameter of the nanofiber as a benchmark, deviation of the surface equivalent mobility approximation was quantified. An empirical equation was developed for high aspect ratio non-spherical particles in terms of $Kn(d_A)$ and the sphericity. The actual mobility diameter can then be evaluated. Particle rotational relaxation time, defining the time it takes for particles to reach the “orientation-averaged” state, is also discussed. It should be noted that, while it is reasonable accurate, the equivalent surface mobility diameter is by no means theoretically rigorous. However, the presented method provides a fast and convenient approach to evaluate high aspect ratio non-spherical particle mobilities. It will be of significant value to experimental and high aspect ratio non-spherical particle characterization.

Particle drag

Spherical particle drag

Assuming creeping flow, in the continuum regime, Stokes law describes the resistance of a spherical particle in a viscous fluid as

$$F_{DC} = 3\pi\mu Ud, \quad [1]$$

where μ is dynamic viscosity of the fluid, U is slip velocity, and d is diameter of the particle. Friction factor $3\pi\mu d$ is a function of fluid viscosity and particle geometry. In the free molecular regime where particle dynamic

is governed by gas kinetic theory, Epstein (1923) derived particle resistance as a consequence of momentum transfer between particle-molecule collisions. That is,

$$F_{DM} = \frac{4\pi\mu Ud}{3Kn} \left(1 + \alpha \frac{\pi}{8}\right), \quad [2]$$

here α is particle momentum accommodation coefficient, $Kn = 2\lambda/d$ is the Knudsen number, and λ is gas mean free path. In view of a smooth transition from continuum friction to molecular resistance, Cunningham correction C_c was derived by Cunningham (1910) and Millikan (1923) and applied to the continuum Stokes drag to prescribe the particle resistance in entire flow regimes. That is,

$$F_D = \frac{F_{DC}}{C_c} = \frac{3\pi\mu Ud}{C_c}. \quad [3]$$

Here C_c is (Davies 1945)

$$C_c = 1 + \frac{2\lambda}{d} \left(1.257 + 0.4e^{(-1.1d/2\lambda)}\right). \quad [4]$$

It is seen in Equation (4) that C_c is a function of gas mean free path λ , particle diameter d , and consequently of Knudsen number Kn . As $Kn \gg 1$, F_D of Equation (3) approaches that of Equation (2).

Non-spherical particle drag

Continuum regime

For non-spherical particles, a dynamic shape factor is frequently introduced to express the Stokes drag in a modified form. That is,

$$F_{DC} = 3\pi\mu Ud_L K, \quad [5]$$

where d_L is a characteristic diameter, and K is a correction factor frequently called “dynamic shape factor.” It should be noted that Equation (5) is slightly modified from the original definition (Fuchs 1964; Stober 1971; Hinds 1999) by expanding d_L from volume equivalent diameter to a more general form of a characteristic diameter. Shape factor K is well defined for a limited number of regular-shaped particles. An example is the elongated ellipsoid with the lateral diameter of d_L , for which it is defined as (Jeffery 1922; Oseen 1927)

$$K_{\perp} = \frac{8(\beta^2 - 1)}{3 \left\{ [(2\beta^2 - 3)\ln(\beta + \sqrt{\beta^2 - 1})/\sqrt{\beta^2 - 1}] + \beta \right\}}, \quad [6]$$

and

$$K_{\parallel} = \frac{4(\beta^2 - 1)}{3 \left\{ [(2\beta^2 - 1) \ln(\beta + \sqrt{\beta^2 - 1}) / \sqrt{\beta^2 - 1}] - \beta \right\}}. \quad [7]$$

Here $K_{\perp}$ and $K_{\parallel}$ represent the “dynamic shape factors” of the ellipsoid in lateral and principal directions, respectively. β in Equations (6) and (7) is the aspect ratio (ratio of the length to lateral diameter). Brenner (1963) gave the dynamic shape factor of a thin disk of diameter d_L in direction of its axis as $8/(3\pi)$. For a long cylinder of diameter d_L and length l , Burgers (1938) obtained the dynamic shape factor for its motion parallel to the long axis as

$$K_{\parallel} = \frac{2}{3d_L [\ln(2\beta) - 0.72]}. \quad [8]$$

For majority of the irregular shaped particles, general expression for K is not available. Instead, non-spherical drag corrections were obtained by conducting free-fall tests in sedimentation tanks and compare to that of a volume equivalent sphere. For this method, Tran-Cong et al. (2004) proposed an empirical drag coefficient C_D for non-spherical particles of irregular shapes as

$$C_D = \frac{24}{Re} \frac{d_A}{d_{ev}} \left[1 + \frac{0.15}{\sqrt{c}} \left(\frac{d_A}{d_{ev}} Re \right)^{0.687} \right] + \frac{0.42 \left(\frac{d_A}{d_{ev}} \right)^2}{\sqrt{c} \left[1 + 4.25 \times 10^4 \left(\frac{d_A}{d_{ev}} Re \right)^{-1.16} \right]}. \quad [9]$$

Here Re is the Reynolds number based on volume equivalent diameter d_{ev} , d_A is the equivalent projected area diameter (in direction of the particle motion), defined as

$$d_A = \sqrt{4A_p/\pi}, \quad [10]$$

In Equation (10), A_p is the project area of particle in direction of its motion. c in Equation (9) is particle circularity, defined as

$$c = \frac{\pi d_A}{P_p}. \quad [11]$$

In Equation (11), P_p is the projected perimeter of the particle in direction of its motion. Stokes drag is then calculated as:

$$F_{DC} = \frac{1}{2} C_D \rho U^2 A_p. \quad [12]$$

Here ρ is fluid density. Though not explicitly specified, relationship of the dynamic shape factor K and the drag coefficient C_D can be derived. Here, the characteristic diameter d_L in Equation (5) is taken as d_{ev} . Particle Reynolds number in the range of 0.15 to 2000, circularity of 0.4 to 1.0, and d_A/d_{ev} from 0.80 to 1.50 were covered in the experiments (Tran-Cong et al. 2004). Similar studies were reported by Horvath (1974), Lasso and Weidman (1986), and Haider and Levenspiel (1989), among others.

Free molecular regime

Explicit expression for non-spherical particle resistance in free molecular regime is scarce. Dahneke (1973a) derived the free molecular resistance of non-spherical disks, cylinders, spheroids, and cubes of positive curvatures. General form of the free molecular resistance is

$$F_{DM} = \frac{1}{2} \pi \mu U d_L K'. \quad [13]$$

Here K' is a shape-dependent coefficient. For an elongated ellipsoid, K' (in principal and lateral directions) is expressed as

$$K'_{\perp} = \frac{\beta}{Kn} \left\{ E_p \left[4 + \left(\frac{\pi}{2} - 1 \right) \alpha \right] + \frac{G_p}{F_p^2} \left(2 + \frac{4F_p^2 + \pi - 6}{4} \right) \alpha \right\}, \quad [14]$$

and

$$K'_{\parallel} = \frac{\beta}{Kn} \left\{ 2E_p \alpha + \frac{G_p}{F_p^2} \left(F_p^2 (4 - 2\alpha) - 4 + \left(3 - \frac{\pi}{2\beta^2} \right) \alpha \right) \right\}, \quad [15]$$

where

$$E_p = \frac{\sin^{-1} F_p}{F_p}, \quad F_p = \sqrt{1 - \frac{1}{\beta^2}}, \quad G_p = \frac{1}{\beta} - E_p. \quad [16]$$

For a thin disk and a long cylinder, the shape factors in direction of particle axis are

$$K' = \frac{1}{Kn} \left(\frac{\pi - 4}{2} \alpha + 4 \right) \quad [17]$$

and

$$K' = \frac{1}{Kn} \left[\left(2\beta + \frac{\pi}{2} - 2 \right) \alpha + 4 \right], \quad [18]$$

respectively.

In above equations, Kn is defined on the characteristic diameter d_L . A limited number of well-defined d_L is given as the diameter, lateral diameter, and side length for disks, cylinders, spheroids, and cubes of positive curvatures. d_L of other irregular shapes depends on the specific application and the most representative characteristic lengths for particle dynamics. Based on the kinetic theory of ion transport in gases (Mason and McDaniel 1988), and measurements in a combined tandem ion mobility spectrometry-mass spectrometry (IMS-MS; Hogan and Fernández de la Mora 2011), the free molecular resistance for an arbitrary-shaped particle can be approximated as (Zhang et al. 2012)

$$F_{DM} = 2.67 \frac{\mu}{\lambda} \zeta A_p U. \quad [19]$$

Here A_p is the orientation-averaged projected area, ζ is the momentum scattering coefficient, for which a value of 1.36 is recommended in most circumstances.

Unlike in the continuum regime, there is no reported measurement of dynamic shape factors for non-spherical particles in free molecular regime.

Transition regime

A complete formulation of non-spherical transition resistance was given by Dahneke (1973b) by using an “adjusted sphere” method. Applying a slip correction similar to Cunningham correction for a sphere, the method ensures an accurate representation of particle resistance in the free molecular and continuum regimes, and at the same time, achieves a smooth slip transition. Cc maintains the same form as that of the sphere; however, with independent variable, diameter, as that of the “adjusted sphere” (d_{adj}). Particle resistance in the entire flow regime is given as

$$F_D = \frac{F_{DC}}{Cc(d_{adj})} = \frac{3\pi\mu U d_L K}{Cc(d_{adj})}. \quad [20]$$

Here $Cc(d_{adj})$ is

$$Cc(d_{adj}) = 1 + \frac{d_L}{d_{adj}} Kn (1.257 + 0.4e^{\frac{-1.1 d_{adj}}{Kn d_L}}). \quad [21]$$

In Equation (21), d_L is the particle characteristic diameter, Kn is the Knudsen number ($2\lambda/d_L$), and d_{adj} is the diameter of the “adjusted sphere.” Apparently, d_L and d_{adj} can only be determined for the limited number of regular-shaped particles in both the free molecular and continuum regimes: they are disks, cylinders, spheroids, and cubes of positive curvatures. Fan and Ahmadi (2000) derived d_{adj} for an elongated ellipsoid as

$$d_{adj\perp} = \frac{1.657 d_L \beta}{16(\beta^2 - 1)} (A \cdot B) \quad \text{and} \quad d_{adj\parallel} = \frac{1.657 d_L \beta}{8(\beta^2 - 1)} (C \cdot D), \quad [22]$$

where

$$A = \frac{2\beta^2 - 3}{\sqrt{\beta^2 - 1}} \ln \left(\beta + \sqrt{\beta^2 - 1} \right) + \beta, \quad [23]$$

$$B = E_p \left[4 + \left(\frac{\pi}{2} - 1 \right) \alpha \right] + \frac{G_p}{F_p^2} \left(2 + \frac{4F_p^2 + \pi - 6}{4} \right) \alpha, \quad [24]$$

$$C = \frac{2\beta^2 - 1}{\sqrt{\beta^2 - 1}} \ln \left(\beta + \sqrt{\beta^2 - 1} \right) - \beta, \quad [25]$$

$$D = 2E_p \alpha + \frac{G_p}{F_p^2} \left[F^2 (4 - 2\alpha) - 4 + \left(3 - \frac{\pi}{2\beta^2} \right) \alpha \right]. \quad [26]$$

The “adjusted sphere” method has been supported by experiments (Cheng et al. 1988; Rogak et al. 1993), and most recently validated by Melas et al. (2014, 2015) by using the Collision Rate Method (CRM), and Zhang et al. (2012) by using the Direct Simulation Monte Carlo (DSMC) Method.

For majority of the irregular-shaped particles, such as fractal-like agglomerates and straight chains, d_{adj} is not available due to the lack of free molecular information. As a convenience, Equation (4) together with a volume equivalent diameter d_{ev} , is frequently used to approximate the slip correction.

Controversies of the non-spherical particle resistance calculation

There are three outstanding controversies arising from the non-spherical particle resistance approximation. The first controversy is the lack of free molecular information

for majority of the irregular-shaped particles. The second controversy is the slip correction approximation. Slip correction is intended to ensure a smooth transition between the free molecular and continuum regimes; therefore, the lack of information at either end disrupts the resolution. Use of Equation (4) instead of Equation (21), and the selection of d_{ev} in place of d_{adj} also leads to additional inaccuracy. The third controversy is the definition of d_L , the characteristic diameter, in Equation (5) for irregular-shaped particles. While it is appropriate to use d_{ev} as the characteristic diameter in the sedimentation tests, usage of d_{ev} in place of a mobility diameter to characterize the dynamic parameter, such as Re in Equation (9), might not be the most accurate.

Equivalent diameters for non-spherical particles

Due to the lack of an established theory, classification of non-spherical particles is frequently resolved by treating them as spheres with equivalent macroscopic properties. The well-established spherical theory is then applied to these equivalent spheres for particle dynamic analysis.

Volume equivalent sphere

Volume equivalent diameter is defined as the diameter of a sphere with the same volume as that of a non-spherical particle. That is,

$$d_{ev} = \sqrt[3]{\frac{6Vol}{\pi}}. \quad [27]$$

Surface equivalent sphere

Surface equivalent diameter is defined as the diameter of a sphere with the same surface area as that of a non-spherical particle. That is,

$$d_{es} = \sqrt[2]{\frac{A}{\pi}}. \quad [28]$$

It should be noted that A in Equation (28), A_p 's in Equations (12) and (19) are two different quantities.

Aerodynamic equivalent sphere

Aerodynamic diameter is defined as the diameter of a sphere with unit density attaining the same settling velocity in a quiescent fluid as the actual particle under consideration. In view of the equilibrium between the drag and gravitational force, aerodynamic diameter is

defined as

$$d_a = d_{ev} \sqrt{\frac{\rho_p}{\rho_0 \chi}}. \quad [29]$$

Here ρ_p is the particle density, ρ_0 is unit density (1000 kg/m³), and χ is the dynamic shape factor when characteristic diameter is d_{ev} in Equation (5). For a prolate spheroid, χ is given as (Stober 1972; Tian and Ahmadi 2012)

$$\chi = \frac{3K_{\perp}K_{\parallel}}{K_{\perp} + 2K_{\parallel}}, \quad [30]$$

Equivalent stokes (relaxation time) sphere

Particle relaxation time is defined as the time required for a particle to adjust its velocity to the new environment. For a spherical particle, the relaxation time τ is

$$\tau = \frac{d^2 \rho_p^2 Cc}{18\mu}. \quad [31]$$

τ is related to the particle settling velocity and Stokes number, these are,

$$U = \tau g \quad [32]$$

and

$$Stk = \frac{\tau}{l} u. \quad [33]$$

Here u and l are the characteristic fluid velocity and length scale, respectively. Accordingly, the relaxation time equivalent sphere is defined as the sphere achieving the same response time as that of a non-spherical particle in fluid. This is also called equivalent Stokes sphere. For an ellipsoid of revolution, the equivalent Stokes (relaxation time) sphere is given by Shapiro and Goldenberg (1993) and Fan and Ahmadi (1995), respectively, as

$$d_{stk_Shapiro} = d_L \sqrt{\frac{\beta \ln(\beta + \sqrt{\beta^2 - 1})}{\sqrt{\beta^2 - 1}}} \quad [34]$$

and

$$d_{stk_Fan} = d_L \sqrt{\frac{3\beta}{2K_{\perp} + K_{\parallel}}}. \quad [35]$$

Electrical mobility equivalent sphere

For charged particles in a constant electric field, the equilibrium of electrical and frictional forces is frequently

used to characterize particle mobility. Given the singly charged mobility (Z_p), the electrical mobility diameter (d_m) for a sphere is expressed as

$$Z_p = \frac{ze \left[1 + \frac{2\lambda}{d_m} (1.257 + 0.4e^{-1.1\frac{d_m}{2\lambda}}) \right]}{3\pi\mu d_m}. \quad [36]$$

Here z and e are the integer charge state and unit electron charge. Accordingly, the equivalent electrical mobility sphere for a non-spherical particle is defined as the sphere achieving the same drift velocity as that of the particle with the same charge in a constant electric field. From a combination of kinetic theory of ion transport in gases (Mason and McDaniel 1988), the collision limited reaction rate theory (Gopalakrishnan et al. 2011), bipolar diffusion charging analysis (Gopalakrishnan et al. 2015b), and measurements in a combined tandem ion mobility spectrometry–mass spectrometry (IMS-MS) (Hogan and Fernández de la Mora 2011), the mobility diameter for a non-spherical particle can be expressed as (Gopalakrishnan et al. 2015b)

$$Z_p = \frac{ze \left[1 + \frac{\lambda\pi R_s}{A_p} (1.257 + 0.4e^{-1.1\frac{A_p}{\lambda\pi R_s}}) \right]}{6\pi\mu R_s}, \quad [37]$$

where R_s is the particle Smoluchowski radius (Gopalakrishnan et al. 2011). For nanorods and nanotubes, R_s can be expressed in the following form (Gopalakrishnan et al. 2015b):

$$R_s = \left(\frac{3}{16} d_L^2 l \right)^{\frac{1}{3}} (1.0304 + 0.0193x + 0.06229x^2 + 0.00476x^3 + 0.00166x^4 + 2.66 \times 10^{-6}x^7) \quad [38]$$

Here d_L and l are the diameter and length of the rod, and x equals to $\ln(l/d_L)$. In Equation (37), Kn is defined as $\lambda\pi R_s/A_p$, first presented by Rogak and Flagan (1992). Detailed analytical derivation can be found in the work of Zhang et al. (2012) and Melas et al. (2015).

Diffusion equivalent sphere

From Brownian diffusion point of view, Tian et al. (2016) examined the isotropic and anisotropic diffusion property of a nanofiber in relation to its coupled rotational behavior. Based on this study, all fibers with a time scale greater than its relaxation to isotropy time exhibits isotropic macroscopic diffusion. Orientation-averaged diffusion coefficient was then developed, and the corresponding diffusion equivalent sphere diameter

was given as (Tian et al. 2016)

$$d_{\text{diff}} = \frac{d_L \cdot Cc(d_{\text{diff}})}{2(\frac{1}{K_{\hat{x}\hat{x}}} + \frac{1}{K_{\hat{y}\hat{y}}} + \frac{1}{K_{\hat{z}\hat{z}}})}. \quad [39]$$

Here d_L is the fiber lateral diameter, $Cc(d_{\text{diff}})$ is the Cunningham correction, $K_{\hat{x}\hat{x}}$, $K_{\hat{y}\hat{y}}$, and $K_{\hat{z}\hat{z}}$ are the fiber translational dyadic elements (Tian et al. 2016). It is worth to note that $K_{\hat{x}\hat{x}}$, $K_{\hat{y}\hat{y}}$, and $K_{\hat{z}\hat{z}}$ contain fiber orientation-dependent translational slip correction factors given in Tian and Ahmadi (2016b).

Comments on the equivalent diameters

The volume equivalent diameter (d_{ev}), surface equivalent diameter (d_{es}), and projected-area equivalent diameter (d_A) are geometric properties that are independent of particle dynamics in the various flow regimes. The aerodynamic equivalent diameter (d_a) is defined in the continuum regime where particle inertia is significant and the equilibrium is achieved by the balance of the gravity and frictional forces. However, in transition and free molecular regimes where Brownian force is dominant, defining a diameter based on equilibrium between the gravitational and frictional forces loses its meaning. As a result, traditionally defined aerodynamic equivalent diameter (d_a) cannot be used to characterize particle motion in high Knudsen number flows. Similarly, the use of equivalent Stokes (relaxation time) diameter (d_{stk}), which is defined in view of an inertial particle response time, for characterizing particles in the high Knudsen number flows is debatable. The electrical mobility equivalent diameter for a charged particle is derived from the equilibrium between particle electrical force in a constant electric field and the frictional force in a viscous fluid; therefore, the applicability is flow regime independent and can be used in all flow regimes. The diffusion equivalent diameter (d_{diff}) is derived from the Brownian diffusion perspective; therefore, it is expected to be applicable to the characterization of particle dynamics in the transition and free molecular regimes.

It is worth mentioning that, the aerodynamic equivalent sphere diameter given by Equation (29), the equivalent Stokes sphere diameters given by Equations (34) and (35) were shown to be comparable for characterizing particle dynamics in the inertia regime (Tian and Ahmadi 2012; Feng 2012).

Results and discussion

In this study, the air properties are: temperature $T = 293$ K, dynamic viscosity $\mu = 1.84 \times 10^{-5}$ Ns/m², and

air density $\rho = 1.23 \text{ kg/m}^3$. Carbon fibers and nanorods with density of 2560.5 kg/m^3 , diameters of 1, 10, 100, and 1000 nm, and aspect ratios of 3 to 1000 are considered. To test the limiting case of the fiber (rod) approaching a sphere, an aspect ratio of 1 is also included. The various equivalent diameters are calculated and compared, and the most appropriate mobility diameters for high Knudsen particle are identified. Corresponding critical parameters for such characterization are also discussed.

In this study, the gas molecule and particle surface interaction mode in the high Knudsen number flow assume: (1) Maxwell-Boltzmann velocity distribution of the gas molecules striking the particle; (2) 90% of diffusive reflection and 10% of specularly reflection; and (3) particle velocity is considerably smaller than the gas molecule velocity. In addition, since nanofibers and nanorods are convex in geometry, the impinging gas molecules are not affected by reflected molecules and no section of the particle surface is shielded.

Comparison of the equivalent diameters

By using a differential mobility analyzer (DMA), Gopalakrishnan et al. (2015a,b) measured the mobility of modest-to-high aspect ratio particles in the transition and free molecular regimes. The measured mobility diameters for high aspect ratio thin nanotubes (6 to 7 nm diameters and 85 to 105 aspect ratios), and modest aspect ratio medium sized nanorods (11 to 43 nm diameters, 2 to 15 aspect ratios) are used as the benchmark to examine the accuracy of various equivalent diameters as shown in Figure 1. It should be noted that the measured experimental data have a spread up to

40% and only the mean value is displayed. For the high aspect ratio thin nanotubes, Figure 1a compares the predicted equivalent diameters while Figure 1b shows the percent deviation to quantify the accuracy. It is seen from Figures 1a and b that, when compared to the experimental measurement, the diffusion equivalent diameter as given by Equation (39), surface equivalent diameter of Equation (28), and the projected-area equivalent diameter of Equation (10) show the highest accuracy (lowest percent deviations). At high aspect ratios ($\beta > 100$), the differences of these predicted equivalent diameters compared to that of the experiment are less than 3.5%. At an aspect ratio of 85.3, the differences are 10.3% for the diffusion equivalent diameter, 14.6% for the surface equivalent diameter, and 6.0% for the projected-area equivalent diameter, respectively. The predicted electrical mobility equivalent diameter of Equation (37) is slightly higher than the experimental value with about 20%–30% differences. On the other hand, the volume equivalent diameter of Equation (27) and the equivalent Stokes diameter of Equation (35) are much smaller than the measured mobility diameters with differences of 38% to 47% and 67% to 74%, respectively.

For the modest aspect ratio medium sized nanorods, Figure 1c compares the predicted equivalent diameters and Figure 1d quantifies the deviation. Figures 1c and d shows that the predicted electrical mobility equivalent diameter as given by Equation (37) is closest to the experiment with a difference less than 0.8% except for one group of nanorods of 11.2 nm diameter and 4.3 aspect ratio that shows a 25% difference. The diffusion equivalent diameter of Equation (39), surface equivalent diameter of Equation (28), and the projected area equivalent diameter of Equation (10) show the next level of

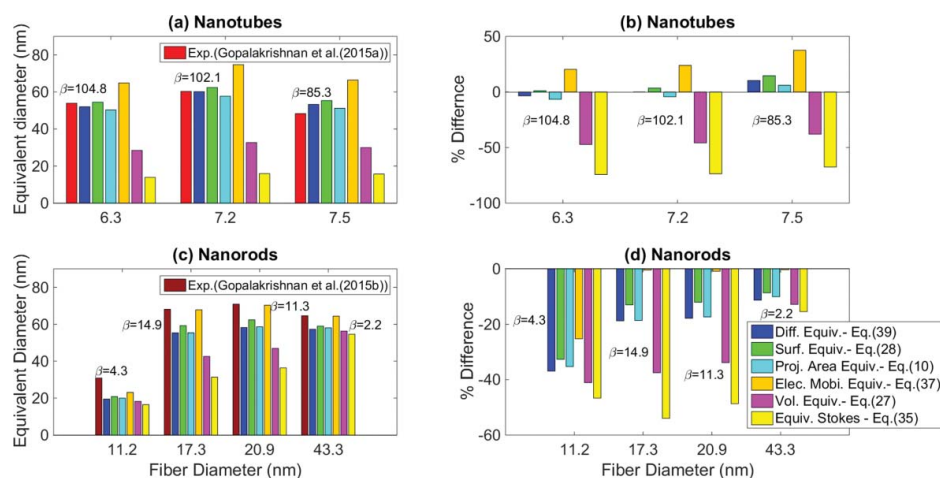


Figure 1. Comparison of the equivalent diameters: (a) for thin nanotubes; (b) percentage differences to the experiment (Gopalakrishnan et al. 2015a); (c) for medium sized nanorods; (d) percentage difference to the experiment (Gopalakrishnan et al. 2015b).

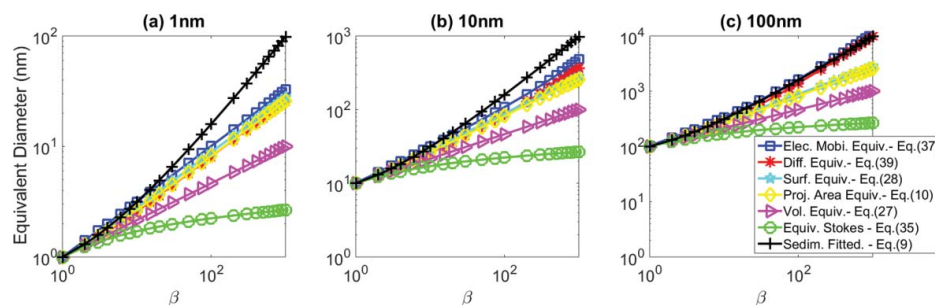


Figure 2. Comparison of the various equivalent diameters to the particle mobility diameter (nanofiber/nanorods).

accuracy with differences of 11% to 19%, 9% to 33%, and 10% to 35%, respectively. For the volume equivalent and equivalent Stokes diameters, minimum accuracy is seen (with the differences of 13% to 41% and 15% to 54% to that of the experiment, respectively). It is also seen that, for the modest aspect ratio medium sized nanorods, all the predicted equivalent diameters are smaller than the experimental measurement, and the difference of various equivalent diameters is the lowest (<15%) for nanorod with a diameter of 43.3 nm and aspect ratio of 2.2.

Comparison with the experimental measurement shown in Figure 1 identifies the most accurate mobility equivalent diameters for the elongated nanoparticles, that are the diffusion equivalent diameter given by Equation (39), electrical mobility equivalent diameter given by Equation (37), surface equivalent diameter given by Equation (28) and the projected-area equivalent diameter given by Equation (10). Figure 2 extends the comparison to a broader dimension including the diameters of 1, 10, 100 nm, and aspect ratios of 1 to 1000. It is clear that, when the aspect ratio approaches unity, the limiting case of a sphere is reached. Though not defined in the transition and free molecular regimes, experimental fitted drag coefficient in a sedimentation tank (e.g., Equation (9), Tran-Cong et al. 2004) is frequently used for non-spherical nanoparticles (Tian et al. 2016). To test the validity, the equivalent diameter derived from Equation (9) is added for comparison (Figure 2).

For the 1 nm nanofibers (tubes) with aspect ratios from 1 to 1000, Figure 2a shows that the predicted equivalent diameters are in the range of 1 to 98.2 nm. The electrical mobility diameter, diffusion equivalent diameter, surface equivalent diameter, and the projected-area equivalent diameter (group 1) are the closest. Compared to diffusion equivalent diameter, the differences are less than 19.7%, 8.7%, and 3.4%, respectively. The volume equivalent and equivalent Stokes diameters are markedly lower with the differences up to 69.4% and 91.8% when compared to the

diffusion equivalent diameter. The sedimentation fitted diameter of Equation (9) shows good agreement with the first group up to an aspect ratio of 20. As the aspect ratio increases beyond 20, sedimentation fitted diameter becomes considerably larger. In general, variations among the different equivalent diameters are increasing with increasing particle aspect ratio. For 10 nm nanofibers (rods), Figure 2b shows that the deviations of the predicted equivalent diameters in group 1 are increasing with the differences up to 23.9%, 31.2%, and 42.5%. However, the sedimentation fitted diameter has less deviation from group 1. For the 100 nm nanofibers (rods), Figure 2c shows that while the surface equivalent diameter deviation increases, sedimentation fitted diameter follows the diffusion equivalent and electrical mobility diameters closely. Furthermore, at 100 nm, the diffusion equivalent and electrical mobility diameters are closer to each other and their differences are <17.1%. Figure 2 also shows that at an aspect ratio of unity, all the equivalent diameters approach the limiting case of a sphere as expected. As the aspect ratio increases, deviations of the predicted equivalent diameters also increase.

Equivalent diameter for high aspect ratio non-spherical nanoparticles

For the more general class of high aspect ratio particles, explicit formula, such as those given by Equations (39) and (37), are not available. Earlier analysis has identified the surface-dominated diameters (surface equivalent and equivalent projected-area diameters) as relatively accurate approximation for characterizing high aspect ratio particle mobility (as is seen in all cases shown in Figure 1 and selected regions in Figure 2). This can be explained with Figure 3 where two different particle-molecule collision scenarios are illustrated in a high Knudsen and continuum regimes. In the high Knudsen regime (Figure 3a), due to the extreme relative length scales between particle size and gas mean free

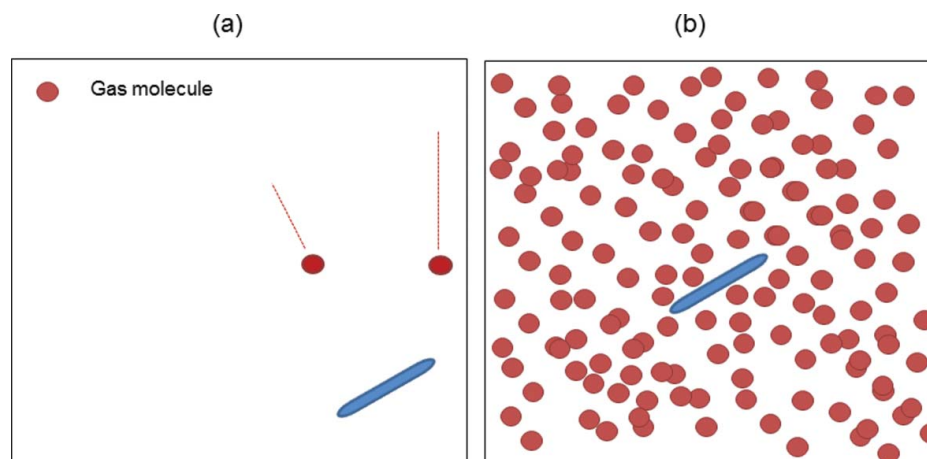


Figure 3. Particle-molecule collision scenarios: (a) high Knudsen regime; (b) continuum regime.

path, particle-molecule collisions can be viewed as point collisions where effect of the particle morphology can be neglected. Particle mobility is best characterized by a parameter most closely describing the collision probability, and the surface area or projected area is the best choice. As a result, the surface-dominated diameters are the appropriate mobility diameters for particles in high Knudsen regime. On the other hand, particle-molecule collisions in a continuum regime (Figure 3b) occur in a close proximity to the particle; therefore, surface feature of the morphology cannot be neglected. As expected, accuracy of the surface-dominated diameter approximation reduces as the Knudsen number $Kn(d_L)$ decreases. This is supported by Figure 2 that, as the particle diameter increases from 1 to 100 nm, deviation of the surface-dominated diameters to that of the diffusion and electrical mobility equivalent diameters increase steadily.

Figure 4 displays the percentage deviation between the equivalent projected area and the diffusion equivalent diameters when characterizing nanofibers of 1 to

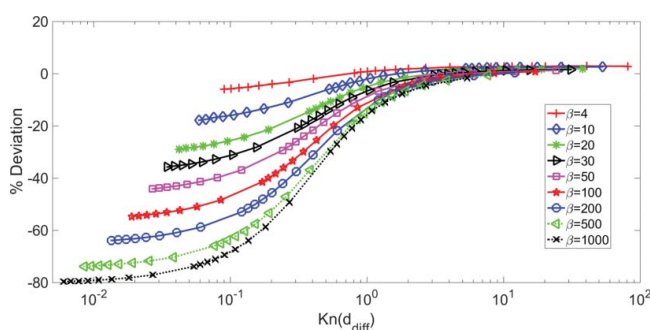


Figure 4. Accuracy of mobility characterization by using the surface equivalent diameters (Benchmark: Equation (39) of the elongated particles).

900 nm in diameter and 4 to 1000 in aspect ratios. Since the diffusion equivalent diameter of Equation (39) is theoretically rigorously derived and shown to be in good agreement with the experiment (Gopalakrishnan et al. 2015a,b), it is used as the benchmark. Percentage deviation to the benchmark is plotted against $Kn(d_{diff})$ and the particle aspect ratio. Figure 4 clearly shows the insensitivity of particle mobility diameter at high Knudsen numbers to the particle aspect ratio. When $Kn(d_{diff}) \geq 5$, it is seen that the deviation in mobility approximation approaches zero, shape induced variation in particle mobility vanishes, and a projected area equivalent diameter universally characterizes the particle mobility. This applies to all aspect ratios including the extreme case of $\beta = 1000$. For $Kn(d_{diff}) < 5$, the shape-induced variation in particle mobility diameter appears and increases with a decrease in $Kn(d_{diff})$. Based on the data in Figure 4 (including the extreme case of $\beta = 1000$), for a bandwidth of 10% of accuracy, $Kn(d_{diff}) > 1.4$ is required. When the deviation relaxed to 20% and 30%, $Kn(d_{diff}) > 0.8$ and 0.5 are needed. At low $Kn(d_{diff})$ (< 5), higher aspect ratio implies higher mobility deviation when using the projected area equivalent diameter, and it generally underestimates the particle mobility diameter. Data in Figure 4 are for elongated particles. Whether the analysis can be extended to general non-spherical particles, further investigate is needed. Current result is in very good agreement with the projected area approximation for particle agglomerates in the free molecule and transition flows presented by Rogak et al. (1993). A recent work of Melas et al. (2015), by using the Collision Rate Method on straight chain agglomerates, implies the validity of the free molecule expression for $Kn(d_L) > 2$, which is very close to the current findings.

Instead of the aspect ratio, particle sphericity can be used to assess deviation of the projected area equivalent diameter to the actual mobility diameter for high aspect ratio nanoparticles at low $Kn(d_A)$. It is also seen from Figure 4 that, in the limiting case of a sphere, the projected area equivalent and the mobility diameters are identical.

To facilitate the estimate of particle mobility, an expression is fitted to data shown in Figure 4, where the percentage deviation of the particle projected area equivalent diameter to benchmark is given as

$$\begin{aligned} \% \text{ deviation} &= (a \cdot e^{b \cdot Kn(d_A)} + c \cdot e^{d \cdot Kn(d_A)} + 3) / 100. \\ a &= 74.6\Phi^3 - 218.37^2 + 246.3\Phi - 102.57 \\ b &= 2.781\Phi^3 - 4.134\Phi^2 + 0.6266\Phi - 2.058 \\ c &= -68.34\Phi^3 + 104.1\Phi^2 - 34.42\Phi - 6.681 \\ d &= 0.4581\Phi^3 - 0.3156\Phi^2 - 0.5512\Phi - 0.02191 \end{aligned} \quad [40]$$

In Equation (40), particle sphericity Φ is defined as

$$\Phi = \frac{\pi^{1/3}(6Vol)^{2/3}}{A}. \quad [41]$$

Particle sphericity is a measure of how the non-spherical particles deviate from spheres. It was first defined by Wadell (1933), and then used by Pettyjohn and Christensen (1948), Haider and Levenspiel (1989), Hartman and Yates (1993) to characterize the shape of isometric non-spherical particles. Equation (41) should be applied to $Kn(d_A) < 1.4$ according to Figure 4.

Applicability of Equation (40)

Equation (40) applies to particles of isotropic macroscopic translational properties (or particles without a preferred orientation). Tian et al. (2016) defined a relaxation time τ_{ri} for a fiber to exhibit an isotropic macroscopic translational diffusion. This is also the relaxation to isotropy time for an ensemble of fibers initially with the same orientation. For fiber of ellipsoid, τ_{ri} is given as (Tian et al. 2016)

$$\tau_{ri} = 100 \cdot \min \left\{ \frac{32\pi^3 \mu a^2}{3\kappa \vartheta} (K_x^r, K_y^r, K_z^r) \right\}. \quad [42]$$

Here a is the semi-minor axis ($a = d/2$), κ is the Boltzmann constant, and ϑ is the absolute temperature. K_i^r is the fiber rotational resistance coefficients given by Tian et al. (2016). Translating Equation (42) into high aspect ratio non-spherical particles, τ_{ri} can be

expressed in terms of $Kn(d_A)$ and sphericity as

$$\begin{aligned} \tau_{ri} &= 100 \cdot e^{p1 \cdot (\ln(Kn(d_A)))^3 + p2 \cdot (\ln(Kn(d_A)))^2 + p3 \cdot \ln(Kn(d_A)) + p4} \\ p1 &= 0.9294\Phi^5 - 1.954\Phi^4 + 1.337\Phi^3 - 0.2748\Phi^2 \\ &\quad + 0.0003883\Phi - 0.02056 \\ p2 &= 13.29\Phi^5 - 39.98\Phi^4 + 46.41\Phi^3 - 25.85\Phi^2 \\ &\quad + 6.895\Phi - 0.7215. \\ p3 &= -1.27\Phi^5 + 3.355\Phi^4 - 3.721\Phi^3 + 2.747\Phi^2 \\ &\quad - 1.897\Phi - 2.226 \\ p4 &= 18.23\Phi^5 - 55.37\Phi^4 + 68.13\Phi^3 - 45.49\Phi^2 \\ &\quad + 20.04\Phi - 12.81 \end{aligned} \quad [43]$$

For nanofibers of 1 and 100 nm diameters, 1000 and 10 aspect ratios ($Kn(d_A) = 5.34$ and $\Phi = 0.127$, $Kn(d_A) = 0.498$ and $\Phi = 0.588$), the estimated τ_{ri} is in the order of 10^{-5} and 10^{-1} s, respectively. As the particle size increases ($Kn(d_A) < 0.1$), inertia and particle morphology start to play important role. In this regime, the aerodynamic equivalent diameter and the equivalent Stokes (or relaxation time) diameter can be used to characterize the particle mobility.

Applicability to aerosol agglomerates

Though derivation in this study assumes convex particle shape, it is interesting to investigate whether the presented method can be applied to aerosol agglomerates that contain an important class of non-spherical particles present in many systems (e.g., combustion fumes, atmospheric aerosols, and nano-agglomerates). Aerosol agglomerates are frequently modeled as cluster of spheres with the same or varying sizes, and the surface morphology contains convex sections where it is partially shielded from the impinging gas molecules. Onto the shielded surface, the reflected gas molecules could have subsequent collisions.

By using then Monte Carlo method, Chan and Dahneke (1981) derived the free-molecule drag on straight chain of uniform spheres. The friction resistance (of the straight chain) over the entire Knudsen regime was given by an adjusted sphere method connecting the continuum and free molecular formulations. Extending the result, Lall and Friedlander (2006) described a mathematical model to calculate the mobility diameters, number, surface area, and volume distribution of low fractal aggregates (fractal dimension < 2) in an electrical mobility analyzer. The primary particle size in these aggregates should be much smaller than the gas mean free path. Separately, Rogak et al. (1993) investigated the mobility and

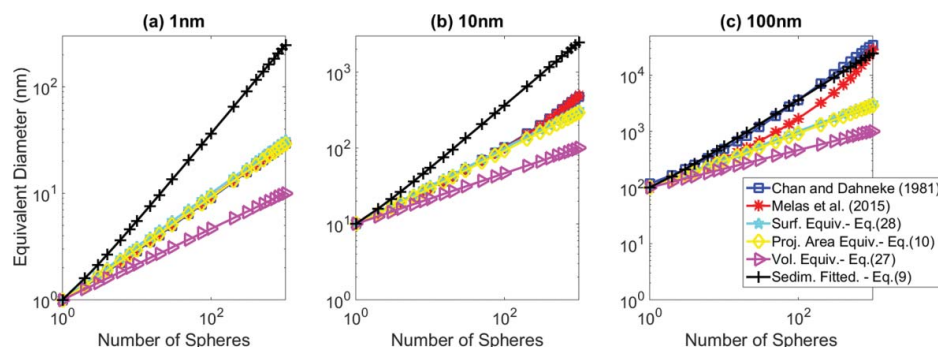


Figure 5. Comparison of the various equivalent diameters to the particle mobility diameter (straight chain agglomerates).

structure of aerosol agglomerates. An observation of a nearly identical mobility diameter and equivalent projected-area diameter was noted in the free molecular regime. A remarkable continued correlation between the agglomerates' mobility and the equivalent projected-area diameters was observed throughout the transition regime. More recently, by using the Collision Rate Method (CRM), Melas et al. (2014, 2015) described a method of calculating friction coefficient and mobility radius of the fractal-like aggregates in the transition regime.

To evaluate the current finding in application to low fractal-dimension aggregates, Figure 5 compares the various equivalent diameters for straight chain agglomerates containing 1 to 1000 spheres (with fixed primary spheres of 1, 10, and 100 nm in diameter). In the free molecular regime (primary sphere of 1 nm, Figure 5a), the mobility diameters of Chan and Dahneke (1981) and Melas et al. (2015), the surface equivalent diameter, and projected-area equivalent diameter overlap. Differences to Chan and Dahneke's (1981) mobility diameter are shown to be less than 3.2%, 10.7%, and 2.4% for the mobility diameter of Melas et al. (2015), surface equivalent, and projected-area equivalent diameters, respectively. The projected-area equivalent diameter is shown to be extremely accurate for free molecular regime mobility characterization, while the volume equivalent and

sedimentation fitted diameters are shown to be far off. The $Kn(d_{Dahneke})$ based on Chan and Dahneke's (1981) mobility diameter is from 4.8 to 140.0 for the straight chains shown in Figure 5a. The same trend continues in Figure 5b for the straight chains containing 10 nm primary spheres up to 100 spheres ($Kn(d_{Dahneke}) > 1.4$). Beyond that, both the surface and projected-area equivalent diameters deviate away from Chan and Dahneke's (1981) mobility diameter. The mobility diameter of Melas et al. (2015) still shows considerable accuracy ($<3.1\%$ difference) up to 1000 spheres. The volume equivalent and sedimentation fitted diameters remain the least accurate. When the primary sphere increases to 100 nm (Figure 5c, $Kn(d_{Dahneke}) < 1.0$), interestingly, Chan and Dahneke's (1981) mobility diameter and the sedimentation fitted diameter overlap, while a slight deviation was observed with the mobility diameter of Melas et al. (2015). Surface and projected-area equivalent diameters clearly departed from that of the Chan and Dahneke's (1981). Derivations of the presented mobility diameters (for the straight chain agglomerates) in Figure 5 can be found in the online supplemental information (SI).

Figure 5 confirmed the current finding that the projected-area equivalent diameter is a fairly accurate mobility diameter for high aspect ratio non-spherical

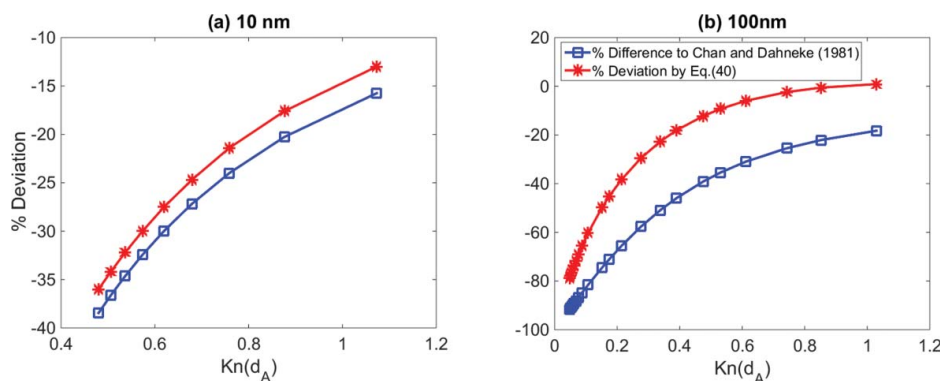


Figure 6. Accuracy of mobility characterization by using the projected area equivalent diameters.

Table 1. Equivalent diffusion diameter of nanorods—comparison with the experiment.

d (nm)	Length (nm)	β	Experiment	d_{diff} (nm) (Equation (39))			
				$Cc(d_{\text{diff}})$	Cc_{avg}	$Cc(d_{\text{ev}})$	No Cc
17.3	257.0	14.9	68.1	55.3	72.5	69.5	75.8
20.9	232.0	11.3	70.9	58.3	72.4	70.1	75.5
11.2	47.4	4.3	30.9	19.5	21.2	20.8	21.9
43.3	94.9	2.2	64.6	57.3	58.8	58.1	59.5

Table 2. Equivalent diffusion diameter of nanotubes—comparison with the experiment.

d (nm)	Length (nm)	β	Experiment	d_{diff} (nm) (Equation (39))			
				$Cc(d_{\text{diff}})$	Cc_{avg}	$Cc(d_{\text{ev}})$	No Cc
6.3	659.99	104.76	53.9	52.02	115.20	89.55	120.85
7.2	734.98	102.08	60.3	60.17	129.66	102.02	135.98
7.5	639.98	85.33	48.3	53.30	113.53	89.20	119.01

nanoparticles in high Knudsen number flow. By applying Equation (40), the % deviation is calculated and compared to that of Chan and Dahneke (1981) (Figure 6). Here the comparison is limited to agglomerates of $Kn(d_A) < 1.4$ (accordingly to the discussion on Figure 4). It is seen in Figure 6 that the overall trend of variation and magnitude generally agree. However, a consistent underestimation by Equation (40) is observed, which appears to be related to the primary sphere size. Figure 6 implies that Equation (40) can be used for quick deviation estimation in the transition regime. However, further experimental, theoretical, and numerical investigations are needed for more refined analysis and understanding.

The slip correction

As discussed in earlier section, slip correction is the second outstanding “unknown” for accurate dynamic characterization of the non-spherical particles. In the work of Tian et al. (2016), three different approximations of $Cc(d_{\text{diff}})$ were used for calculating the fiber diffusion equivalent diameter with Equation (39). These are:

- (1) With Cc on the right-hand side of Equation (39) being approximated as the averaged slip correction:

$$Cc_{\text{avg}} = \frac{1}{3}(C_x^t + C_y^t + C_z^t), \quad [44]$$

here C_i^t 's are the orientation-dependent translational slip-correction factors of the fiber (Fan and Ahmadi 2000; Tian et al. 2016). Further detail on derivation of C_i^t can be found in the work of Tian and Ahmadi (2016b);

- (2) With Cc on the right-hand side of Equation (39) being approximated as $Cc(d_{\text{ev}})$;

- (3) Without considering Cc on the right-hand side of Equation (39). It should be noted that, in this case, C_i^t 's in the denominator of Equation (39) should be removed as well.

The direct solution of $Cc(d_{\text{diff}})$ from Equation (39), without using any approximation by using a numerical scheme, was also included for comparison. When compared with the experiment of Gopalakrishnan et al. (2015b) (for low-to-moderate aspect ratio nanorods), $Cc(d_{\text{ev}})$ shows the highest accuracy while the approximation of the other two methods are within 5% and 10% proximity (Table 1). $Cc(d_{\text{diff}})$ is shown to be the least accurate.

To further investigate the accuracy of using different Cc 's, Table 2 shows a comparison of the predicted d_{diff} (Equation (39)) with above methods to the measured mobility diameter for high aspect ratio nanotubes (Gopalakrishnan et al. 2015a). It is seen from Table 2 that direct solution of $Cc(d_{\text{diff}})$ (from Equation (39)) leads to the most accurate prediction, while other approximations generally over predict d_{diff} . Among all approximations, $Cc(d_{\text{ev}})$ generates the closest prediction. In summary, $Cc(d_{\text{diff}})$ is the most accurate for high aspect ratio nanotubes, while $Cc(d_{\text{ev}})$ brings the best result for nanotubes of low-to-moderate aspect ratios. Since $Cc(d_{\text{diff}})$ is the direct solution from Equation (39) (without any approximation), why it does not yield the most accurate solution for low-to-moderate aspect ratio particles need further experimental, theoretical, and numerical investigations.

Conclusions

In this study, the orientation-averaged mobility of high aspect ratio non-spherical particles (with no preferred alignment) in high Knudsen number flows was examined. By comparing the predicted equivalent diameters

to the experimental and theoretical values for benchmark particles, a surface-dominated mobility in high Knudsen flow was identified. For particles with $Kn(d_L) \geq 5$, the projected area equivalent diameter can be used to characterize the particle mobility for high aspect ratio non-spherical particles. Accuracy of this approximation reduces with a decrease of $Kn(d_L)$, and an empirical equation is developed to quantify the deviation. As the particle size increases ($Kn(d_L) < 0.1$), the inertia and particle morphology start to play important roles. In this regime, aerodynamic and Stokes (or relaxation time) diameters should be used to characterize the particle mobility.

The study also analyzed the applicability of the sedimentation fitted diameters for high aspect ratio non-spherical particles in high Knudsen number flows. It was found out that, at diameters of 1 and 10 nm, the approximation is reasonable up to an aspect ratio of 20 (or $\Phi > 0.469$). At 100 nm diameter, the approximation is reasonable for all aspect ratio (or sphericity) particles.

The presented study is extremely useful for fast characterization of high aspect ratio non-spherical particle mobilities. The characterization accuracy is Knudsen number related. Further experimental, theoretical, and numerical investigations would be necessary for improved accuracy and validation with non-spherical particles of all morphologies.

Funding

The financial support provided by the National Institute for Occupational Safety and Health (NIOSH) through grant R01 OH003900 is gratefully acknowledged.

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