Drag force, diffusion coefficient, and electric mobility of small particles.
I. Theory applicable to the free-molecule regime

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The transport of small particles in the free-molecule regime is investigated on the basis of gas kinetic theory. Drag force formulations were derived in two limiting collision models—namely, specular and diffuse scattering—by considering the potential force of interactions between the particle and fluid molecules. A parametrized drag coefficient equation is proposed and accounts for the transition from specular to diffuse scattering as particle size exceeds a critical value. The resulting formulations are shown to be consistent with the Chapman-Enskog theory of molecular diffusion. In the limit of rigid-body interactions, these formulations can be simplified also to Epstein's solutions [P. S. Epstein, Phys. Rev. **23**, 710 (1924)].

I. INTRODUCTION

Aerosols represent a class of materials of interest to a wide range of research disciplines, including atmospheric science [1], materials processing [2], chemically reacting flows, and combustion [3]. Particle transport properties, such as drag force, diffusion coefficient, and electric mobility [4], in low-density gases are critical to the measurement and prediction of the nucleation and dynamics of nanoparticles. Particle transport also plays an important role in the manipulation of nanomaterials and nanostructures in gas media.

There have been many attempts in obtaining a generalized treatment for particle motion in a fluid. However, the theory is far from complete. The situation is manifested by a sharp contrast between the ease with which the electric mobility of particles is measured [5] and difficulties in interpreting the mobility-based particle size. Evidence shows that the mobility diameter differs from the diameter measured by electronic microscopy [6,7], yet the relation between the two diameters remains unclear. The lack of a satisfactory fundamental theory of nanoparticle transport translates into added difficulties in explaining such phenomena as particle nucleation and growth in flames, as recently discussed by Zhao *et al.* [8,9].

In the present paper, we offer a review of the theory of particle transport with a focus on the motion of small, spherical particles in low-density gases (Sec. II). We consider here the drag force due to the relative motion of the particle and fluid, the diffusion, and the electric mobility of particles, although other particle transport mechanisms, including thermophoresis and diffusiophoresis, may prove to be equally important especially in reacting gases [3]. From a comparison of the various theories and considerations of the gas kinetic theory and dynamics of molecular collisions, it will become apparent that none of the theories developed for small-particle transport in low-density gases should be considered as being complete. In Sec. III, we propose a generalized theory for drag force of particles in the free-molecule regime. In Sec. V, we demonstrate that this generalized theory unifies various particle transport theories. The application of this theory is discussed in a companion paper [10], hereafter referred to as paper II.

II. REVIEW OF PARTICLE TRANSPORT THEORIES

In 1851, Stokes [11] solved the equations of motion of a rigid sphere in a fluid in the laminar regime. Stokes' analysis yielded the much celebrated formula for the drag on a sphere of radius R moving steadily in a fluid with velocity $\mathbf{V}$. Under the stick boundary condition, the drag formula takes the form of

$$\mathbf{F}_0 = -6\pi\mu R\mathbf{V}, \qquad (1)$$

where μ is the viscosity of the fluid, R is the particle radius, and $\mathbf{V}$ is the relative velocity vector between the particle and the fluid (the minus sign denotes the opposite orientations of $\mathbf{F}$ and $\mathbf{V}$). Later, Einstein [12] showed that the Brownian diffusion coefficient D was related to its drag coefficient k_d by $D = kT/k_d$. Recognizing that the drag coefficient is related to the drag force as $k_d = -(\mathbf{F}_0/\mathbf{V})$, the Stokes-Einstein relation is obtained as

$$D_0 = \frac{kT}{6\pi\mu R}. \qquad (2)$$

In 1910, Cunningham [13] recognized that the stick boundary condition in Stokes' derivation is valid only for the continuum regime where the Knudsen number $\mathrm{Kn} = \lambda/R \ll 1$. Here, λ is the mean free path of the fluid, $\lambda = (\sqrt{2}\pi\sigma_g^2 N)^{-1}$, σ_g is the collision diameter of the fluid molecule, and N is the number density of the gas. An empirical correction factor, known as the Cunningham factor, was introduced as

$$C(\mathrm{Kn}) = 1 + A'\mathrm{Kn}, \qquad (3)$$

where A' is a parameter. The resulting Stokes-Cunningham equation takes the form of

$$\mathbf{F} = -\frac{6\pi\mu R\mathbf{V}}{C}. \qquad (4)$$

Later, Knudsen and Weber [14] realized that the parameter A' is a constant only for small values of Kn and proposed a correction factor for all Kn. Equation (4) resulting from this revision takes the form of

TABLE I. Published values of Cunningham slip correction parameters (adapted mostly from Allen and Raabe [26]).

Author	Mean free path λ (μm)	A	B	E	$A+B$
Knudsen and Weber [14]	0.09417	0.772	0.40	1.63	1.172
Millikan [19]	0.09417	0.864	0.29	1.25	1.154
Langmuir [20]	0.133	0.62	0.22	2.20	0.84
Davies [21]	0.066	1.257	0.40	1.10	1.657
DeMarcus and Thomas [22]	0.0655	1.25	0.44	1.09	1.690
Reif [23]	0.0652	1.26	0.45	1.08	1.710
Fuchs [24]	0.0653	1.246	0.42	0.87	1.666
Dahneke [25]	0.066	1.234	0.414	0.87	1.648
Allen and Raabe [26]	0.0673	1.155	0.471	0.596	1.626
Buckley and Loyalka [27]	—	1.099	0.518	0.425	1.617

$$\mathbf{F} = -\frac{6\pi\mu R\mathbf{V}}{1 + \mathrm{Kn}[A + B\exp(-E/\mathrm{Kn})]}, \qquad (5)$$

where A, B, and E are constants. The above equation is known as the Stokes-Cunningham formula and has been extensively used in modern instrumentation for particle size and mobility measurements (e.g., [15,16]).

The determination of the parameter values in the Cunningham correction began with the classical work of Millikan [17–19], who measured the mobility of a large number of oil droplets. Over the years, Millikan's data remain the core data used in fitting the values of A, B, and E [20–27]. Table I summarizes the results of these studies. It is seen that since the work of Davies [21], the $A+B$ value has converged to a narrow range of 1.6–1.7. The significance of this value will be discussed later.

Equation (5) simplifies to the original Stokes' equation (1) for the continuum region with $\mathrm{Kn}\ll1$, where the drag force is proportional to R. In the free-molecule region ($\mathrm{Kn}\gg1$), the equation becomes

$$\mathbf{F}_\infty = -\frac{6\pi\mu R^2\mathbf{V}}{\lambda(A+B)}, \qquad (6)$$

where the subscript ∞ denotes the large-Kn limit [and, likewise, the subscript 0 in Eqs. (1) and (2) denotes the small-Kn limit]. In the large-Kn limit, the drag force assumes an R^2 dependence. Figure 1 depicts schematically the variation of k_d/R ($= -\mathbf{F}_0/R\mathbf{V}$) as a function of the particle radius (or Knudsen number). The transition from small- to large-Kn limits may be viewed as the fall off of k_d/R as a function of the Knudsen number, as given by the Cunningham correction (dashed line).

Using the gas-kinetic theory, Epstein [28] obtained that in the free-molecule regime the force due to relative motion of a particle in gas is given by

$$\mathbf{F}_\infty = -\frac{8}{3}\delta\sqrt{2\pi m_g kT}NR^2\mathbf{V}, \qquad (7)$$

where δ is a numerical factor that depends on the model of reflection of the molecules from the surface of the sphere, e.g., $\delta=1$ and $(8+\pi)/8$ for the limiting cases of specular and diffuse scattering, respectively, as shown in Fig. 1. In Eq. (7), m_g is the mass of the gas molecule, and k is the Boltzmann constant. The diffuse-scattering result was also reproduced by Wang-Chang [29]. Millikan [19] noted that his data for $\mathrm{Kn}\gg1$ could be well explained with a linear combination of Epstein's diffuse and specular scattering results, i.e.,

$$\mathbf{F}_\infty = \varphi\mathbf{F}_{\infty,\mathrm{diffuse}} + (1-\varphi)\mathbf{F}_{\infty,\mathrm{specular}}$$

$$= -\frac{8+\pi\varphi}{3}\sqrt{2\pi m_g kT}NR^2\mathbf{V}, \qquad (8)$$

and suggested that $\varphi\sim0.9$. Allen and Raabe [26] recommended a similar φ value, equal to 0.914. Following Epstein's analysis, a number of attempts were made to solve the Boltzmann equation and its variations in the transition regime [30–33]. These studies are, however, beyond the scope of the present discussion.
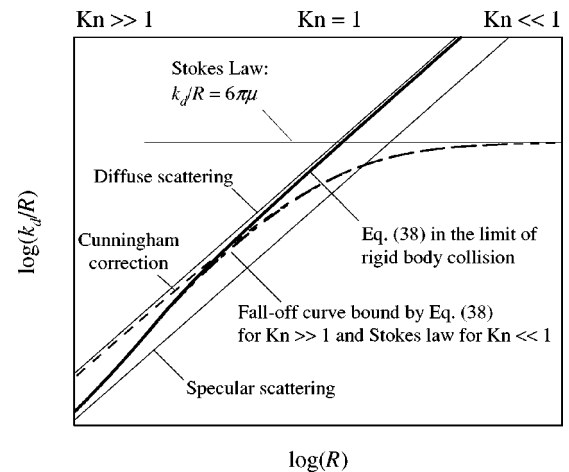

FIG. 1. Schematic illustration of the drag coefficient for a rigid body.

In the limit of Kn≫1, the limitation of the Cunningham correction can be explained in the context of Epstein's equations. Putting the expression of viscosity [34,35],

$$\mu = \frac{5}{16} \frac{\sqrt{\pi m_g kT}}{\pi \sigma^2 \Omega^{(2,2)*}}, \qquad (9)$$

into Eq. (6), we obtain the Stokes-Cunningham drag force as

$$\mathbf{F}_\infty = -\frac{15\pi}{8(A+B)\Omega^{(2,2)*}} \sqrt{2\pi m_g kT} N R^2 \mathbf{V}. \qquad (10)$$

Here $\Omega^{(2,2)*}$ is the reduced collision integral [35]. Taking $\varphi = 0.9$ [19], a comparison of Eqs. (8) and (10) gives

$$A+B = \frac{1.632}{\Omega^{(2,2)*}}. \qquad (11)$$

The dependence of $A+B$ on $\Omega^{(2,2)*}$ is translated into dependences on temperature and the nature of the gas molecules. Since $\Omega^{(2,2)*}$ roughly scales with $T^{-1/2}$, the empirical Cunningham correction is expected to be predictive only under the condition of Millikan's experiments, i.e., particle motion in air at room temperature, where $\Omega^{(2,2)*}$ happens to be about unity. Under this condition $A+B \approx 1.632$, which validates the range of $A+B$ values given in Table I.

A further limitation of the empirical Cunningham slip correction may be noted here. The smallest oil droplets in Millikan's experiments are of the size of ~ 0.3 μm, which is far too large to validate the accuracy of the slip correction for particles of a few nanometers in diameter. Millikan's oil droplet data and its resulting slip correction are shown to be consistent with Epstein's diffuse scattering model, yet as a particle approaches the size of a molecule, the scattering process becomes specular, as evidenced by the success of the Chapman-Enskog theory of molecular diffusion. In the limit of rigid-body collisions, the Stokes-Cunningham formula tends to overpredict the drag force of small, nanosized particles, as depicted in Fig. 1. This claim is supported by recent experimental evidence that the mobility diameter based on the Cunningham slip correction is about 20% larger than the value measured by transmission electronic microscopy [6,7].

The limitation of the Epstein theory is also well understood as the particle approaches the molecular size. This limitation arises from the rigid-body collision assumption. Elastic scattering due to long-range intermolecular forces is known to be prevalent for molecular diffusion [34]. The long-range forces include the van der Waals interactions and, when the particle is charged, the ion-induced dipole interactions (e.g., [36]).

According to the Chapman-Enskog theory [34], the first approximation of the drag coefficient is given by $k_d = (8/3)\sqrt{2\pi m_r kT} N \sigma^2 \Omega^{(1,1)*}$, and the corresponding drag force is

$$\mathbf{F}_\infty = -\frac{8}{3} \sqrt{2\pi m_r kT} N \sigma^2 \Omega^{(1,1)*} \mathbf{V}, \qquad (12)$$

where m_r is the reduced mass of the gas molecule and particle, $m_r = m_g m_p /(m_g + m_p)$, and m_p is the mass of the particle. Comparing Eq. (12) with Epstein's equation (7), we see that Epstein's specular-reflection result is a special case of the Chapman-Enskog theory, where $\Omega^{(1,1)*} = 1$ for rigid-body collisions and $m_p \gg m_g$. For large particles, the rigid-body model is adequate, because of negligible influence of the particle-molecule forces, as evidenced by the close agreement between Millikan's data and Epstein's diffuse-scattering formulation. As particle approaches the molecular size, however, the potential forces will exert some influence on the scattering process and, thus, the particle transport properties.

The effects of the long-range potential forces have been discussed in the context of ion mobility [37] and were recognized by the recent study of Tammet [38]. Furthermore, Rudyak and Krasnolutski [39] treated the nanoparticle diffusion coefficient on the basis of the Chapman-Enskog theory. Both studies offer evidence that Epstein's equations are inaccurate as particles approach the molecular size.

Last, we note that although the Chapman-Enskog formulation is theoretically rigorous, it accounts for specular-type scattering and, therefore, is applicable to small particles only. The transition from specular-type scattering to diffuse scattering is expected to occur at a particle mass diameter of a few nanometers [38]. A validated theoretical treatment for this transition is not available.

There have been recent attempts to develop alternative formulations [38,40–47]. A summary of the formulations relevant to the free molecule regime is given in Table II. The most rigorous and sophisticated treatment to date is perhaps that of Tammet [38], who considered both the transition of the scattering models from small to large particles and the influence of the potential force of interactions (see Table II). In other cases, the revised drag force formulas are either too cumbersome to be useful or do not fully address the problems discussed above.

It is the objective of the current study to derive a generalized theory of particle transport in low-density gases in the Kn≫1 regime. Our derivation is made on the basis of gas-kinetic theory. We consider, for the first time, the influence of van der Waals and other interactions on the drag force. Our derivation keeps the restriction of low Reynolds number and, as before, assumes the specular- and diffuse-scattering models as limiting cases. On the basis of these theoretical results, we discuss the model of transition from specular to diffuse scattering and propose a parametrized model for the drag coefficient that is simple and useful. The validation of this theory will be presented in paper II [6].

III. GENERALIZED THEORY FOR DRAG FORCE IN THE Kn≫1 REGIME

Consider a gas in local equilibrium with center-of-mass velocity equal to 0. Let the velocity of the random motion of the gas molecules be $\mathbf{v}$. A particle is introduced into the gas with an instantaneous drift velocity $\mathbf{V}$. Upon collision between the particle and a gas molecule, the velocities of the

TABLE II. Selected drag coefficient formulations in the Kn≫1 regime.

Author	Formulation (k_d)	Comments
Cunningham [13]	$\dfrac{6\pi\mu R}{1+A'\mathrm{Kn}}$	Empirical correction to Stokes' law.
Knudsen and Weber [14]	$\dfrac{6\pi\mu R}{1+\mathrm{Kn}[A+Be^{-E/\mathrm{Kn}}]}$	Empirical correction to Stokes' law. Parameters A, B, and E are expected to depend on temperature and the nature of the fluid.
Epstein [28]	$\dfrac{8}{3}\delta\sqrt{2\pi m_g kT}NR^2$	Based on the gas-kinetic theory and the rigid-body collision model. δ is a numerical factor ($\delta=1$ for specular-elastic scattering and $(1+\pi/8)$ for diffuse scattering).
Cercignani and Pagani [40,41]	$\dfrac{2}{3}\sqrt{2\pi m_g kT}NR^2\left(\dfrac{3\mathrm{Kn}^2\mathrm{stat}J}{\pi^{3/2}V^2}-4\right)$	J is a variational functional for the drag exerted on a sphere by a rarefied gas.
Friedlander [42]	$\dfrac{8}{3}\left(1+\dfrac{\pi\alpha}{8}\right)\sqrt{2\pi m_g kT}NR^2$	Here the parameter α is the known as the momentum accommodation coefficient. It accounts for the appropriate mixing of specular and diffuse reflections.
Annis et al. [43]	$\dfrac{8\pi\mu R}{3\mathrm{Kn}\Omega^{(1,1)*}}\left(1-\dfrac{\delta\alpha_L}{5}\right)$	Simplified from a three parameter form for Kn≫1. δ is a numerical factor that depends on the scattering model, and α_L is the Lorentzian thermal diffusion factor of the binary gas-particle mixture ($\delta=1$ and $\alpha_L=0.5$ for specular-elastic scattering).
Tammet [38]	$\dfrac{16}{9}\sqrt{2\pi m_r kT}N\delta^2\Omega^{(1,1)}$	$\Omega^{(1,1)}$ is the collision integral given by $s(r_m,T)+\Omega^{(1,1)*}_{\infty-4}-1$, $s(r_m,T)$ is a switch function determined by the reflection law, r_m is the particle mass radius, $\Omega^{(1,1)*}_{\infty-4}$ is the reduced collision integral for elastic-specular interaction of a $\infty-4$ potential function, and δ is the collision distance.
Fernández de la Mora et al. [46]	$\dfrac{8}{3}\left(1+\dfrac{\pi\alpha}{8}\right)\sqrt{2\pi m_g kT}N(R+r_g)^2$	An extension of Friedlander's formula by considering the radius of the gas molecule r_g in the collision cross section. The parameter α is the momentum accommodation factor.
This work	$\dfrac{8}{3}\sqrt{2\pi m_r kT}NR^2\Omega^{(1,1)*}_{avg}$, where $\Omega^{(1,1)*}_{avg}=\varphi\Omega^{(1,1)*}_d+(1-\varphi)\Omega^{(1,1)*}_s$	Based on the gas-kinetic theory and considering the intermolecular potential energy of interactions. The average reduced collision integral is parametrized by the collision integral of specular and diffuse scattering and the momentum accommodation function φ.

particle and gas molecule are altered and denoted by $\mathbf{V}'$ and $\mathbf{v}'$, respectively.

For convenience we shall attach the coordinate system to the particle with the origin O, located at the mass center of the particle, as shown in Fig. 2. Then the velocity of the gas molecules is given by $\mathbf{g}=\mathbf{v}-\mathbf{V}$ before collision and $\mathbf{g}'=\mathbf{v}'-\mathbf{V}'$ after collision. Let the z axis of the coordinate system be parallel to $\mathbf{g}$ and $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ be unit vectors in the x, y, and z directions, respectively. In the coordinate system defined above, the drag on the particle is the time derivative of the momentum of gas molecules. Consider a gas molecule traveling in a cylindrical region with an impact factor b and velocity $\mathbf{g}$ (Fig. 2) and a small sector of this cylindrical shell of an area given by $bdbd\varepsilon$. The number of molecules in this sector at time t is

$$n=fgbdbd\varepsilon dt, \tag{13}$$

where f is the velocity distribution function of gas molecules,

$$f=\frac{N}{(2\pi kT/m_r)^{3/2}}\exp\left(-\frac{v^2}{2kT/m_r}\right). \tag{14}$$

Here the use of the reduced mass in the velocity distribution function is dictated by the reference frame. The total momentum $\mathbf{p}$ of the molecules in the sector is therefore

$$\mathbf{p}=m_r n\mathbf{g}. \tag{15}$$

The momentum of reflected molecules is essentially given by the angle of scattering, assuming that the particle drift velocity is sufficiently small. For specular scattering, the angle of incidence is equal to that of scattering, as shown in Fig. 2, and the magnitudes of $\mathbf{g}$ and $\mathbf{g}'$ are assumed to be equal. For diffuse scattering, the magnitude of $\mathbf{g}'$ is Maxwellian, and the direction of $\mathbf{g}'$ is random above the element surface of impact [18]. In both cases, the dynamics of flyby scattering are identical.

A. Specular scattering

The angle of scattering χ (Fig. 2) is a function of b and the magnitude of $\mathbf{g}$. Let the potential function of interaction be $\Phi(r)$, where r is the center-to-center distance between the gas molecule and particle. The angle of scattering is given by [35]
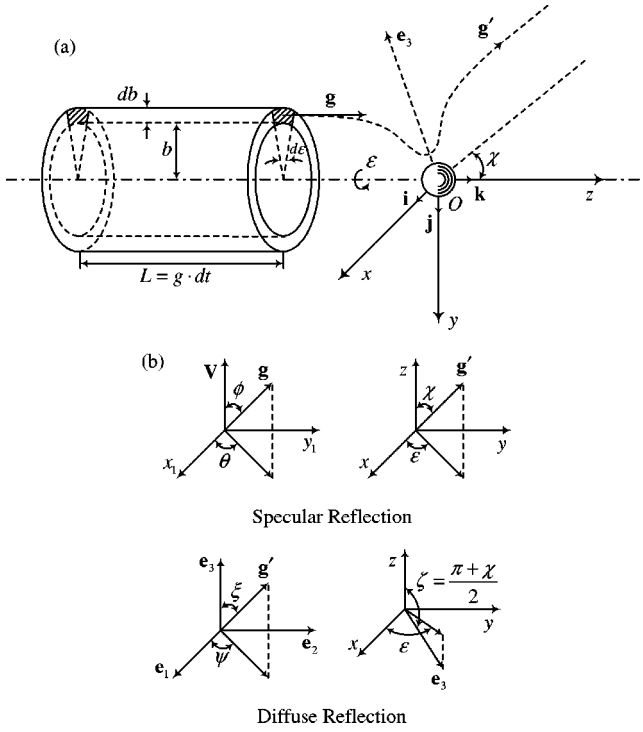
FIG. 2. (a) Collision model and the reference frame. (b) Relationship among various vectors.

$$\chi(g,b)=\pi-2b\int_{r_m}^{\infty}\frac{dr}{r^2\sqrt{1-\frac{b^2}{r^2}-\frac{\Phi(r)}{m_r g^2/2}}}, \quad (16)$$

where r_m is the distance of the closest encounter. The momentum of the reflected molecules is

$$\mathbf{p}'=m_r n g(\mathbf{k}\cos\chi+\mathbf{i}\sin\chi\cos\varepsilon+\mathbf{j}\sin\chi\sin\varepsilon). \quad (17)$$

Here we assume that the momentum magnitude of the scattered molecules is equal to that of the incidence. Since the second and third terms on the right-hand side of Eq. (17) vanish upon integration over ε from 0 to 2π, we only need to consider the first term in $\mathbf{p}'$. In the sector given by $bdbd\varepsilon$, the differential drag force is

$$d\mathbf{F}_{\infty,s}=\frac{\mathbf{p}-\mathbf{p}'}{dt}=m_r n\mathbf{g}(1-\cos\chi). \quad (18)$$

Putting Eqs. (15) and (17) into (18) and integrating, we obtain

$$\mathbf{F}_{\infty,s}=\frac{m_r N}{(2\pi kT/m_r)^{3/2}}\int_{\mathbf{v}}g\mathbf{g}\exp\left(-\frac{v^2}{2kT/m_r}\right)Q_s(g)d\mathbf{v}, \quad (19)$$

where $Q_s(g)$ is the cross section, defined by

$$Q_s(g)=2\pi\int_0^{\infty}(1-\cos\chi)bdb. \quad (20)$$

It is reasonable to assume that the variation in the magnitude of the drift velocity $\mathbf{V}$ is much smaller than that of the gas molecules $\mathbf{v}$. With this assumption, we have $d\mathbf{v}\approx d\mathbf{g}$. Let ϕ and θ be the colatitude and azimuthal angles of $\mathbf{g}$ in a reference frame in which $\mathbf{V}$ is collinear with the z axis (Fig. 2); Eq. (19) can be written as

$$\mathbf{F}_{\infty,s}=\frac{m_r N}{(2\pi kT/m_r)^{3/2}}$$

$$\times\int_{\mathbf{g}}g\mathbf{g}\exp\left(-\frac{g^2+V^2+2gV\cos\phi}{2kT/m_r}\right)Q_s(g)d\mathbf{g}$$

$$=\frac{2\pi m_r N\mathbf{V}}{(2\pi kT/m_r)^{3/2}V}\int_0^{\infty}g^4\exp\left(-\frac{g^2+V^2+2gV\cos\phi}{2kT/m_r}\right)$$

$$\times Q_s(g)dg\int_0^{\pi}\cos\phi\sin\phi d\phi. \quad (21)$$

For $g\gg V$ and $m_p\gg m_g$, we have $kT\sim m_g g^2\sim m_r g^2\gg m_r gV$ and therefore $gV/(kT/m_r)\ll1$. Expanding the exponential term in Eq. (21) yields

$$\exp\left(-\frac{g^2+V^2+2gV\cos\phi}{2kT/m_r}\right)$$

$$\approx\exp\left(-\frac{g^2}{2kT/m_r}\right)\left(1-\frac{gV\cos\phi}{kT/m_r}\right). \quad (22)$$

Putting Eq. (22) into (21) and integrating over ϕ, we obtain

$$\mathbf{F}_{\infty,s}=-\frac{4\pi m_r^2 N\mathbf{V}}{3kT(2\pi kT/m_r)^{3/2}}$$

$$\times\int_0^{\infty}g^5\exp\left(-\frac{g^2}{2kT/m_r}\right)Q_s(g)dg. \quad (23)$$

Let $\gamma=g/\sqrt{2kT/m_r}$, Eq. (23) simplifies to

$$\mathbf{F}_{\infty,s}=-\frac{8}{3\pi}\sqrt{2\pi m_r kT}N\mathbf{V}\int_0^{\infty}\gamma^5\exp(-\gamma^2)Q_s(g)d\gamma. \quad (24)$$

We now define a collision integral as

$$\Omega_s^{(1,1)}=\int_0^{\infty}\exp(-\gamma^2)\gamma^5 Q_s(g)d\gamma. \quad (25)$$

The corresponding drag-force equation is

$$\mathbf{F}_{\infty,s}=-\frac{8}{3\pi}\sqrt{2\pi m_r kT}N\Omega_s^{(1,1)}\mathbf{V}. \quad (26)$$

In Eq. (26), the particle size information is intrinsically imbedded in the collision integral. The particle size is measured, in fact, by the potential energy of interactions between the particle and gas molecule. For convenience and follow-

ing the approach of Chapman-Enskog theory [35], we introduce here a reduced collision integral, defined as

$$\Omega_s^{(1,1)*} = \frac{\Omega_s^{(1,1)}}{\pi R^2}, \tag{27}$$

and the drag-force equation becomes

$$\mathbf{F}_{\infty,s} = -\frac{8}{3}\sqrt{2\pi m_r kT}NR^2\Omega_s^{(1,1)*}\mathbf{V}. \tag{28}$$

Here we choose πR^2 to represent the collision cross section. An alternative choice could be made by using $\pi\sigma_{g-p}^2$, where $\sigma_{g-p}=R+\sigma_g/2$, and σ_g is the collision diameter of the gas molecule, but from the standpoint of applications, the resulting drag equation is more cumbersome to use. We further note that when particles approach the molecular size, the definition of the radius requires some special consideration. While this issue will be specifically discussed in paper II, here the drag force and reduced collision integral equations are rigorous as long as a particle radius exists.

The drag-force equation (28) is identical to the first-order approximation of the Chapman-Enskog theory, i.e., Eq. (12). For large particles, the influence of van der Waals forces between the gas molecule and particle is expected to play a minor role, and the collision can be well described by the rigid body assumption. It can be shown that Eq. (27) is reduced to $\Omega_s^{(1,1)*}=1$ if the rigid-body assumption is made. Consequently, Eq. (28) simplifies to the Epstein equation (7) with $\delta=1$.

B. Diffuse scattering

For diffuse scattering the velocity distribution of scattered molecules is Maxwellian and given by

$$f' = cgf\exp\left(-\frac{g'^2}{2kT/m_r}\right), \tag{29}$$

where c is a constant to be determined and gf is the incident flux. Again the temperature of the scattered molecules is assumed to be equal to that of the incidence. By mass conservation, we obtain $gf=\int_{\mathbf{g}'}g'f'd\mathbf{g}'$ and $c=(m_r/kT)^2/(2\pi)$. The analysis is simplified by recognizing that the effective angle of diffuse scattering is normal to the surface of impact, because the net momentum transfer is zero in the direction parallel to the surface. Define the polar angles between $\mathbf{g}'$ and $\mathbf{e}_3$ as ξ and ψ, where $\mathbf{e}_3$ is a unit vector as shown in Fig. 2. The momentum of the reflected molecules can be written as

$$\mathbf{p}' = bdbd\varepsilon dt\int_{\mathbf{g}'}m_rg'\mathbf{g}'\cos\xi f'd\mathbf{g}'$$

$$= \frac{m_rn\mathbf{e}_3}{(kT/m_r)^2}\int_0^{\infty}g'^4\exp\left(-\frac{g'^2}{2kT/m_r}\right)dg'$$

$$\times\int_0^{\pi/2}\cos^2\xi\sin\xi d\xi. \tag{30}$$

Integrating the above equation, we obtain

$$\mathbf{p}' = \frac{\sqrt{2\pi m_r kT}}{2}n\mathbf{e}_3 = \frac{\sqrt{2\pi m_r kT}}{2}gfbdbd\varepsilon dt\mathbf{e}_3. \tag{31}$$

Decomposing the unit vector $\mathbf{e}_3$ on the principal axes of the coordinate system, we obtain the momentum of the reflected molecule as

$$\mathbf{p}' = \frac{\sqrt{2m_r\pi kT}}{2}[\mathbf{g}\cos\zeta + \mathbf{i}g\sin\zeta\cos\varepsilon + \mathbf{j}g\sin\zeta\sin\varepsilon]$$

$$\times fbdbd\varepsilon dt, \tag{32}$$

where $\zeta=(\chi+\pi)/2$. Putting Eqs. (32) and (15) into Eq. (18) and integrating, we obtain the drag-force equation in the diffuse scattering limit as

$$\mathbf{F}_{\infty,d} = m_r\int_{\mathbf{v}}g\mathbf{g}fd\mathbf{v}\int_0^{\infty}2\pi\left(1+\frac{1}{g}\sqrt{\frac{\pi kT}{2m_r}}\sin\frac{\chi}{2}\right)bdb. \tag{33}$$

It may be noted that the integral $\int_0^{\infty}\sin(\chi/2)bdb$ is divergent. Physically, the divergence is caused by the assumption that the scattering is diffuse even if the gas molecule and particle do not physically collide as the impact parameter b exceeds a critical value. This is, of course, unreasonable. We therefore have to consider three types of molecular scattering upon interactions with the particle, as shown in Fig. 3 [35]. Obviously, diffuse scattering is relevant to contact collision, i.e., type (a), only. Orbiting scattering [type (b)] is possible if $b=b_0$, and scattering must be of type (c), known as the grazing collision, if $b>b_0$, where b_0 is the critical impact factor. The cross section of types (b) and (c) is deterministic and may be calculated from Eq. (20) with the lower integration bound set for b_0.

Equation (33) is revised accordingly as

$$\mathbf{F}_{\infty,d} = 2\pi m_r\int_{\mathbf{v}}g\mathbf{g}fd\mathbf{v}\left[\int_0^{b_0}\left(1+\frac{1}{g}\sqrt{\frac{\pi kT}{2m_r}}\sin\frac{\chi}{2}\right)bdb\right.$$

$$\left. + \int_{b_0}^{\infty}(1-\cos\chi)bdb\right]. \tag{34}$$

We shall define the diffuse-scattering cross section as

$$Q_d(g) = 2\pi\left[\int_0^{b_0}\left(1+\frac{1}{g}\sqrt{\frac{\pi kT}{2m_r}}\sin\frac{\chi}{2}\right)bdb\right.$$

$$\left. + \int_{b_0}^{\infty}(1-\cos\chi)bdb\right]. \tag{35}$$

Combining Eqs. (34) and (35) and integrating, we again obtain the drag-force equation as

$$\mathbf{F}_{\infty,d} = -\frac{8}{3}\sqrt{2\pi m_r kT}NR^2\Omega_d^{(1,1)*}\mathbf{V}, \tag{36}$$
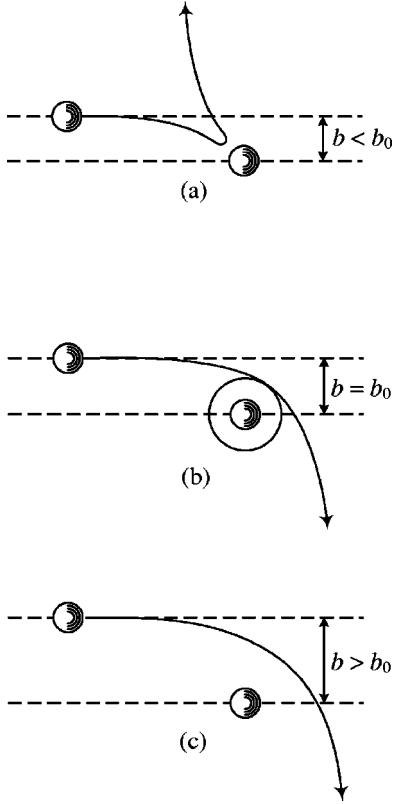
FIG. 3. Scattering type: (a) for $b < b_0$, particles collide with the scattering angle $-\infty < \chi \leqslant \pi$, (b) for $b = b_0$, orbiting scattering occurs and $\chi \rightarrow -\infty$, and (c) for $b > b_0$, grazing scattering takes place and $\chi < 0$.

where $\Omega_d^{(1,1)*}$ is the reduced diffuse-scattering collision integral,

$$\Omega_d^{(1,1)*} = \frac{\int_0^\infty \exp(-\gamma^2)\gamma^5 Q_d(g)\,d\gamma}{\pi R^2}. \tag{37}$$

Comparing the results of specular-type and diffuse scattering model, we see that formulations for the drag force and reduced collision integral are identical. The difference between the two scattering models is manifested only in the formulation of the collision cross section; cf. Eqs. (20) and (35). It can be shown that for rigid-body collisions, the collision integral of Eq. (37) is simplified to $\Omega_d^{(1,1)*} = 1 + \pi/8$. Then, Eq. (36) turns out to be the exact Epstein form of diffuse scattering, as expected for large particles.

C. Parametrization

The derivations described in the preceding sections point to the fact that a generalized particle transport equation can be expressed in terms of an average reduced collision integral, $\Omega_{avg}^{(1,1)*}$. For the drag coefficient, we have

$$k_d = \frac{8}{3}\sqrt{2\pi m_r kT} N R^2 \Omega_{avg}^{(1,1)*}. \tag{38}$$

It is possible to carry out an *ab initio* calculation for $\Omega_{avg}^{(1,1)*}$ using the rigorous approach of molecular dynamics or classical trajectory calculations [37]. In practice, this is not always feasible. For this reason, a parametrized form of $\Omega_{avg}^{(1,1)*}$ is introduced here. Following the approach of Millikan [19], we propose that $\Omega_{avg}^{(1,1)*}$ be parametrized as

$$\Omega_{avg}^{(1,1)*} = \varphi \Omega_d^{(1,1)*} + (1 - \varphi)\Omega_s^{(1,1)*}, \tag{39}$$

where φ ($0 \leqslant \varphi \leqslant 1$) is a switch function. The parametrization accounts for the limiting case of diffuse scattering with $\varphi = 1$ and of specular scattering with $\varphi = 0$. The collision integrals $\Omega_d^{(1,1)*}$ and $\Omega_s^{(1,1)*}$ can be readily calculated if the potential function is known. In a companion paper [10], the collisional integral values are calculated for representative potential functions. The form of the switch function φ will also be developed on the basis of available experimental data.

IV. DIFFUSION COEFFICIENT AND ELECTRIC MOBILITY

We note that Eq. (38) is equally applicable to diffusion coefficient and electric mobility [4]. Thus, the particle diffusion coefficient D can be determined through Einstein's expression [12] as

$$D = \frac{3}{8}\sqrt{\frac{kT}{2\pi m_r}}\frac{1}{N R^2 \Omega_{avg}^{(1,1)*}}. \tag{40}$$

Clearly the above equation is entirely consistent with the Chapman-Enskog treatment of molecular diffusion, with the exception that the reduced collision integral is no longer that of specular scattering.

The electric mobility Z in the limit of zero field is similarly obtained as

$$Z = \frac{3}{8}\frac{q}{\sqrt{2\pi m_r kT} N R^2 \Omega_{avg}^{(1,1)*}}, \tag{41}$$

where q is the charge in the particle. It will be shown in paper II that Eq. (41) is indeed valid when it is compared to available experimental data.

V. DISCUSSION

We shall remark on the parametrized drag force on the basis of the current theoretical treatment. It has been shown that Epstein's equations are special cases of the present results in the limit of rigid-body collisions. Moreover, the results obtained for specular-type scattering or, equivalently, Eq. (38) with $\varphi = 0$ in Eq. (39) are entirely consistent with the Chapman-Enskog's first approximation. Higher approximations are necessary only for the diffusion of small molecular-weight species (e.g., H_2 and He) at very low temperatures [48]. Tammet [38] clearly demonstrated that for particle transport higher-order terms are unnecessary, and the error resulting from neglecting these terms amounts to $<0.1\%$ for $m_p > 5 m_g$.

The formulas of Friedlander [42] and Fernández de la Mora *et al.* [46] (see Table II) are rigid-body limits of Eq. (38). Here we note that the momentum accommodation coefficient in the Friedlander formula is in fact similar to the switch function φ proposed here. The value of this coefficient has been quoted as equal to 0.91 [19,26,42,46], essentially reflecting on the diffuse scattering characteristic of the collision process. As the particle approaches the size of a molecule, we expect that $\varphi \to 0$. Since there is no reason to expect the momentum accommodation coefficient or φ to be a constant over the entire range of particle sizes, we shall hereafter term the function φ as the momentum accommodation function.

Our derivations also validate the formulation of Tammet [38] (Table II), which was extended from the Chapman-Enskog theory. Tammet considered the switch function s to be the reduced collision integral of a rigid sphere. Without charge-induced dipole polarization, the formulation reduces to that of the rigid-body limit. With charge-induced dipole polarization, s is corrected by $\Omega_{\infty-4}^{(1,1)*} - 1$, where $\Omega_{\infty-4}^{(1,1)*}$ is the reduced collision integral for a $(\infty-4)$ potential function.

Last, let us discuss the nature of the momentum accommodation function. In general, φ must be dependent on the particle size. Diffuse reflection may be primarily caused by surface "roughness" and/or by multiple collisions of a gas molecule on the surface of the particle. Larger particles tend to better facilitate multiple collisions because of the larger surface and the greater propensity toward absorbing the translational energy of the gas molecule upon initial impact. The surface roughness, on the other hand, may be effectively reduced due to an increase speed of rotation for small particles.

The expression of the momentum accommodation function will be developed in paper II. Here we note that φ is ~ 0 in the small-particle-size limit and ~ 0.9 in the large-size limit. In the rigid-body limit, this transition causes the k_d/R curve to switch from the specular scattering curve to the diffuse scattering line, as shown in Fig. 1 by the thick solid line. Therefore for small particles the Cunningham correction tends to overpredict k_d/R in the rigid-body limit. The more realistic drag coefficient would be the one that is bound by Eq. (38) for Kn$\gg$1 and the Stokes' law for Kn$\ll$1, as depicted by the dash-dotted-dashed line shown in Fig. 1.

VI. SUMMARY

We investigated the transport of particles in the Kn$\gg$1 regime. Two general formulas were developed for the specular and diffuse scattering on the basis of the gas-kinetic theory. Our derivation considered the influence of potential energy of interactions between the gas molecule and particle. This influence was expressed in terms of the reduced collision integral. On the basis of the theoretical results obtained for the two limiting collision models, the drag coefficient is cast into a parametrized form. A momentum accommodation function was proposed to account for the transition from specular reflections to diffuse scattering due to the increase in particle size. We demonstrated that Epstein's theoretical results can be viewed as the rigid-body limits of the current theoretical formulations. Furthermore, our specular-elastic formulation is completely consistent with Chapman-Enskog's first approximation of molecular diffusion.

[1] J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (Wiley, New York, 1997).

[2] T. T. Kodas and M. J. Hampden-Smith, *Aerosol Processing of Materials* (Wiley, New York, 1998).

[3] D. E. Rosner, *Transport Processes in Chemically Reacting Flow Systems* (Dover, Mineola, NY, 2000).

[4] The drag force **F**, diffusion coefficient D, and electric mobility in the limit of zero field Z are bound by the same drag coefficient, k_d, viz., $\mathbf{F} = -k_d\mathbf{V}$, $D = kT/k_d$, and $Z = q/k_d$, where **V** is the relative velocity vector of a particle moving in a fluid, q is the charge in the particle, k is the Boltzmann constant, and T is the temperature. Therefore, k_d, D, and Z are equivalent attributes of the transport property of a small particle.

[5] G. Kasper, Aerosol Sci. Technol. **1**, 187 (1982).

[6] H. G. Scheibel and J. Porstendörfer, J. Aerosol Sci. **14**, 113 (1983).

[7] V. Ya. Rudyak and S. L. Krasnolutski, Dokl. Phys. **47**, 758 (2002).

[8] B. Zhao, Z. Yang, J. Wang, M. V. Johnston, and H. Wang, Aerosol Sci. Technol. **37**, 611 (2003).

[9] B. Zhao, Z. Yang, M. V. Johnston, H. Wang, A. S. Wexler, M.

Balthasar, and M. Kraft, Combust. Flame **133**, 173 (2003).

[10] Z. Li and H. Wang, following paper, Phys. Rev. E **68**, 061207 (2003).

[11] G. G. Stokes, Proc. Cambridge Philos. Soc. **9**, 8 (1851).

[12] A. Einstein, Ann. Phys. (Leipzig) **17**, 549 (1905).

[13] E. Cunningham, Proc. R. Soc. London, Ser. A **83**, 357 (1910).

[14] M. Knudsen and S. Weber, Ann. Phys. (Leipzig) **36**, 981 (1911).

[15] E. O. Knutson and K. T. Whitby, J. Aerosol Sci. **6**, 431 (1975).

[16] S. Wang and R. C. Flagan, Aerosol Sci. Technol. **13**, 230 (1990).

[17] R. A. Millikan, Science **32**, 436 (1910).

[18] R. A. Millikan, Philos. Mag. **34**, 1 (1917).

[19] R. A. Millikan, Phys. Rev. **22**, 1 (1923).

[20] I. Langmuir, *Filtration of Aerosols and Development of Filter Materials*, OSRD-865 (Office of Scientific Research and Development, Washington, D.C., 1942).

[21] C. N. Davies, Proc. Phys. Soc. London **57**, 259 (1945).

[22] W. DeMarcus and J. W. Thomas, *Theory of a Diffusion Battery*, ORNL-1413 (Oak Ridge National Laboratory, Oak Ridge, TN, 1952), p. 26.

[23] A. E. Reif, *Aviation Medicine Selected Reviews* (Pergamon Press, Oxford, 1958).

[24] N. A. Fuchs, *The Mechanics of Aerosols* (Pergamon Press, Oxford, 1964).

[25] B. E. Dahneke, J. Aerosol Sci. **4**, 139 (1972).

[26] M. D. Allen and O. G. Raabe, J. Aerosol Sci. **13**, 537 (1982).

[27] R. L. Buckley and S. K. Loyalka, J. Aerosol Sci. **20**, 347 (1988).

[28] P. S. Epstein, Phys. Rev. **23**, 710 (1924).

[29] C. S. Wang-Chang (unpublished).

[30] N. A. Fuchs and I. B. Stechkina, Trans. Faraday Soc. **58**, 1949 (1962).

[31] V. C. Liu, S. C. Pang, and H. Jew, Phys. Fluids **8**, 788 (1965).

[32] D. R. Willis, Phys. Fluids **9**, 2522 (1966).

[33] Y. P. Pao and D. R. Willism, Phys. Fluids **12**, 435 (1969).

[34] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, 1970).

[35] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[36] D. D. Huang, J. H. Seinfeld, and W. H. Marlow, J. Colloid Interface Sci. **140**, 258 (1990).

[37] M. F. Mesleh, J. M. Hunter, A. A. Shvartsburg, G. C. Schatz, and M. F. Jarrold, J. Phys. Chem. **100**, 16082 (1996).

[38] H. Tammet, J. Aerosol Sci. **3**, 459 (1995).

[39] V. Ya. Rudyak and S. L. Krasnolutski, Dokl. Phys. **46**, 897 (2001).

[40] C. Cercignani and C. D. Pagani, Phys. Fluids **11**, 1395 (1968).

[41] C. Cercignani and C. D. Pagani, Phys. Fluids **11**, 1399 (1968).

[42] S. K. Friedlander, *Dust, Smoke and Haze* (Wiley, New York, 1977).

[43] B. K. Annis, A. P. Malinauskas, and E. A. Mason, J. Aerosol Sci. **3**, 55 (1972).

[44] L. Ferrari, Chem. Phys. **257**, 63 (2000).

[45] C. M. Sorensen and G. M. Wang, Aerosol Sci. Technol. **33**, 353 (2000).

[46] J. Fernández de la Mora, L. de Juan, K. Liedtke, and A. Schimidt-Ott, J. Aerosol Sci. **34**, 79 (2003).

[47] E. W. McDaniel and E. A. Mason, *The Mobility and Diffusion of Ions in Gases* (Wiley, New York, 1973).

[48] T. R. Marrero and E. A. Mason, J. Phys. Chem. Ref. Data **1**, 1 (1972).