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On the Slip Correction Factor for Simple Gas Molecules Diffusing in Air

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We examine the functional form of the slip correction factor $C(\Pi)$, where Π is a dimensionless group to be determined, for simple (monoatomic, diatomic, and triatomic) gas molecules diffusing in air at normal conditions. We express $C(\Pi)$ in terms of the molecular Reynolds number, $Re_{m_i} = \bar{u}_i d_{k_i}/2\nu_j$, where $\bar{u}_i$ and d_{k_i} are the Maxwell–Boltzmann mean molecular speed and the kinetic diameter of the diffusing gas molecules, and ν_j is the kinematic viscosity of the background gas (dry air). We show that the slip correction is given simply by $C(Re_{m_i}) = Re_{m_i}/Re_{j,\mathrm{ns}}$, where $Re_{j,\mathrm{ns}}$ is a reference no-slip Reynolds number that depends only on the thermodynamic state and viscosity of the background gas j. For dry air at 300 K and 1 atm, $Re_{j,\mathrm{ns}} = 1.36 \times 10^{-5}$, so that $C(Re_{m_i}) = 7.35 \times 10^4 Re_{m_i}$. The approach presented here can be easily generalized to other gas media and leads to a remarkably simple correlation for estimation of Schmidt numbers and binary diffusion coefficients for both stable and unstable trace gases in air. While this correlation depends only on the molecular weight M_i and the number of atoms in the molecule of the diffusing gas, it performs competitively against more complex models.

Nomenclature

$\mathcal{A}$ = model constant in Eq. (12)
a_p = particle radius
$\mathcal{B}$ = model constant in Eq. (13)
$C(\Pi)$ = slip correction factor as a function of dimensionless group Π
$\mathcal{D}_{ij}$ = binary diffusion coefficient for species i diffusing in species j
d_{k_i} = kinetic diameter of species i
e_{ij} = maximum energy of attraction in Lennard–Jones potential [Eq. (11)]
f = friction coefficient in Stokes–Einstein theory [Eq. (2)]
Kn_p = particle Knudsen number [Eq. (3)]
ℓ = mean free path
m = mass of a single molecule
N_{Av} = Avogadro's number, 6.023×10^{26} molecules/kmol
P = pressure
$\mathcal{R}$ = universal gas constant, $8314.5\ \mathrm{J/(kmol \cdot K)}$
$R(\tau)$ = Lagrangian velocity autocorrelation coefficient [Eq. (21)]
$Re_{j,\mathrm{ns}}$ = reference no-slip Reynolds number for background gas species j
Re_{m_i} = molecular Reynolds number for species i
Sc = Schmidt number
T = temperature
$\bar{u}_i$ = mean molecular speed
v = volume of atom or molecule in Fueller et al.'s model
α = collision restitution or momentum accommodation coefficient
ϵ = ratio of molecular masses, M_i/M_j
κ_B = Boltzmann's constant, $1.38 \times 10^{-23}\ \mathrm{J/K}$
μ = dynamic viscosity
ν = kinematic viscosity
ρ = specific mass
σ = collision length (or diameter)
χ_i = shape factor for monoatomic, diatomic, and triatomic molecules
χ_1 = shape factor for monoatomic molecules, 1.00
χ_2 = shape factor for diatomic molecules, 1.23
χ_3 = shape factor for triatomic molecules, 1.39
χ_p = shape factor for nonspherical particles
Ω_μ = collision integral for viscosity and thermal conductivity
$\Omega_{\mathcal{D}}$ = collision integral for binary diffusion

Subscripts

C = proposed model
CE = Chapman–Enskog model
cp = correlation path [Eq. (21)]
Ep = Epstein model
F = Fuller model
i = species i
j = species j (dry air)
p = particle

I. Introduction

THE diffusion of simple monoatomic, diatomic, and triatomic gases in air plays a key role in many biological and physical processes. On the physical side, a number of meteorological, climatological, and aeronautical processes require precise knowledge of binary diffusion coefficients for gas molecules in air [1,2]. For example, industrial processes involving degassing of plastics during thermal processing need to account for multiple gas species for process control and environmental health monitoring [3]. In biological systems, the transport of gas molecules and aerosols trough alveoli and stomata is often controlled by diffusion at air–membrane interfaces [4,5]. Heterogeneous (gas–surface) diffusion to suspended aerosols in the atmosphere is, in some cases, limited by the diffusion of inorganic compounds into the surrounding air. Many critical aspects of atmospheric chemistry are directly affected by these air–surface reactions at the lower atmosphere [6]. Above the homopause, lighter gases segregate gravitationally by diffusion, and the binary

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diffusion coefficients for these unstable trace gases are difficult to measure by conventional methods [7,8].

The general absence of independent experimental data for gas diffusion coefficients in air is often circumvented by classical models given the importance of the above-mentioned process. Well-established models and experimental techniques exist only for a few well-characterized, stable molecules. Tang et al. [6] compiled a list of experimental binary diffusion coefficients for inorganic reactive trace gases of relevance to atmospheric process and compared the experimental values with Fueller's semi-empirical method [9]. The reported agreement was ±30%. Tang et al. [6] conclude that "[t] herefore, in cases where the diffusion of a trace gas has not been measured, Fueller's method can be used to estimate the diffusion coefficient." Earlier, Reid et al. [10] compared results of the Chapman–Enskog (CE) theory with those of Fueller's (F) method against experimental measurements for a wide variety of binary systems and found the agreement between the CE theory and Fueller's method with experiments to be roughly equivalent, with a slight advantage to Fueller's method (7.5% vs 6.9% absolute average errors, respectively). The discrepancy between ±30% and ±7% found in these two studies is explained by the circular contamination of information between experiments and semi-empirical models: model parameters are adjusted to fit experimental results, so the better *characterized* a binary gas system is, the more likely it is to have had its model parameters adjusted to it. Because of this circular inference, model errors for frequently studied stable gases are likely to be substantially smaller than the model errors for less frequently studied gases.

Paradoxically, the binary diffusion coefficients for gases that are critically important to the dynamics of the Earth's atmosphere are still poorly characterized. For example, the diffusion of water vapor in air is not well characterized partially due to the highly polar nature of the water molecule, but perhaps also due to the tendency of water molecules to form molecular clusters [11]. Similarly, the diffusion coefficient of ozone (O_3) in air has never been measured directly [12] until the very recent work by Langerberg and colleagues [8], who used two complementary experimental techniques (arrested flow and twin tube) to study diffusion coefficients of unstable trace gases of atmospheric relevance. Langerberg et al. [8] report systematic errors of the order of 7% for both experimental methods, which the authors consider larger than the 5% systematic error for stable, nonpolar molecules obtained by the CE theory with experimentally adjusted coefficients for the Lennard–Jones potential. They also found that the Fuller's method overestimates the diffusion coefficients of inorganic compounds with a systematic error smaller than 35%, and underestimates the diffusion coefficients of organic compounds with a systematic error of less than 15%. Taking into consideration the relevance of the transfer processes related to water vapor and trace gases in the atmosphere, an analysis that yields a simple estimation for binary diffusion coefficients in air seems in order.

The objectives of this work are as follows: 1) to extend the Stokes–Einstein theory results for aerosols diffusing in air to the molecular scale and, in doing so, to estimate the functional form of the slip correction factor for ideal gas molecules of different shapes and chemical compositions; 2) to compare the results obtained with the newly derived slip correction factor with two of the most reliable semi-empirical models, namely, CE (CE theory with Lennard–Jones 6-12 potential) and F (Fueller's semi-empirical model); 3) to propose a simple physics-based correlation for estimation of Schmidt (Sc_i) numbers and binary diffusion coefficients of polar and nonpolar, stable and unstable trace gases diffusing in dry air with similar uncertainties as those associated with both experiments and the most reliable semi-empirical methods; and 4) to show that the extensive results obtained for aerosol transport in air are compatible with the transport of even the smallest molecules if appropriate slip factor corrections are used.

II. Background

The theory of aerosol diffusion is well-developed and provides accurate results for suspended particles as small as 2 nm (20 Å) in effective diameter [13,14]. The Brownian diffusion of a spherical aerosol particle is expressed in terms of the Stokes–Einstein relation as [13,15]

$$\mathcal{D}_p = \frac{\kappa_B T}{f} \tag{1}$$

where κ_B is the Boltzmann constant (1.38×10^{-23} J/K), T is the absolute temperature of the background gas (bath) in kelvins, and f is the friction coefficient given by [15,16]

$$f = \frac{6\pi\mu a_p \chi_p}{C(\Pi)} = \frac{3\pi\mu d_p \chi_p}{C(\Pi)} \tag{2}$$

where a_p and d_p are the radius and the diameter of the particles, μ is the dynamic viscosity of the suspending gas (in our case dry air), χ_p is a shape factor for nonspherical aerosols, and $C(\Pi)$ is the slip correction factor that accounts for deviations from the continuum regime. As shown in Eq. (2), it is customary to express the slip correction factor $C(\Pi)$ as the ratio between the aerodynamic drag coefficient at the zero Knudsen number Kn_p (continuum) limit, F_0, and the actual aerodynamic resistance exerted on the particle, F_D [17]. Note also that the friction coefficient f in Eq. (2) implies an infinitesimal value for the particle Reynolds number (based on the radius of the particle, a_p, the fluid-to-particle relative velocity, W, and the viscosity of the background gas, ν, such that $Re_p = W a_p/\nu_j \to 0$). Corrections for higher particle Reynolds and Mach numbers are provided in the recent review by Loth and collaborators [18].

Here we define the Knudsen number as

$$Kn_p = \frac{\ell_j}{d_p} \tag{3}$$

where ℓ is the mean free path of the background gas molecules, and d_p is the effective diameter of the diffusing particle (aerosol). The mean free path for air molecules (ℓ_j) is

$$\ell_j = \frac{2\nu_j}{\bar{u}_j} = \nu_j \left(\frac{\pi M_j}{2\mathcal{R}T} \right)^{1/2} \tag{4}$$

where ν_j is the kinematic viscosity of dry air, $\bar{u}_j$ is the mean molecular speed of air molecules given by $\bar{u}_j = \sqrt{8\mathcal{R}/\pi M_j}$, $\mathcal{R}$ is the universal gas constant (8314.5 J/[kmol · K]), and M_j is the mean molecular weight of air molecules (28.96 kg/kmol). Henceforth we assume dry air to behave ideally and to be composed of 78% N_2, 21% O_2, and 1% Ar by volume. The kinematic and dynamic viscosities of dry air at 300 K and 101,325 Pa (1 atm) are assumed to be equal to 1.57×10^{-5} m^2/s and 1.84×10^{-5} kg · m^{-1} · s^{-1}, respectively.

There is no purely mathematical theory for calculating the functional form of the slip correction factor $C(\Pi)$ from the continuum ($Kn_p \to 0$) to the free molecule flow regimes ($Kn_p \to \infty$), but very accurate interpolation functions have been developed over the years with the help of detailed experiments (see, e.g., [19–22]). These correlations are based on the functional form originally proposed by Cunningham [19]:

$$C(Kn_p) = 1 + Kn_p(C_1 + C_2 e^{-C_3/Kn_p}) \tag{5}$$

where often-quoted values of C_n are 2.514, 0.800, and 0.550 for particles diffusing in air [16,20]. Based on Eq. (5), Dahneke [17] used a very clever argument to determine the ratio of the adjusted length scale for nonspherical particles that is valid over the entire range of Kn_p, from continuum (Stokes) to free molecule flows. For particles with aspect ratios of 2 and 3 in free molecule flow, the shape corrections χ_p in Eq. (2) based on the statistical average of all collision orientations in Brownian motion (see, e.g., [13]) are equal to 1.23 and 1.39, respectively (see Table I of Ref. [17]). Because the asymptote for the limit of $Kn_p \to \infty$ is a straight line, we adopt these same values for diatomic and triatomic molecules. In other words, here we assume that the statistically averaged shape factor for all diatomic molecules is $\chi_2 = 1.23$, and for all triatomic molecules is $\chi_3 = 1.39$. We will see that this very simple rule, which originated from extensive studies of small aerosol particles in free molecule flow and only depends on the number of atoms in each molecule, is very effective in predicting the statistically averaged frictional forces acting on nonspherical molecules, regardless of atomic mass ratios of their nuclei.

For very large Kn_p numbers in air, which correspond to either low pressures, high temperatures, or very small aerosols, the friction factor for spherical particles approaches the free molecule expression first derived by Epstein [23] [this is also the limit for $Kn_p \to \infty$ of Eq. (5)]:

$$f_{\mathrm{Ep}} = \frac{2}{3} d_p^2 \rho_j \left(\frac{2\pi\kappa_B T}{m_j} \right)^{1/2} \left[1 + \frac{\alpha\pi}{8} \right] \tag{6}$$

where m_j is the effective mass of a molecule of air, and α is a collision restitution (sometimes referred to as *momentum accommodation*) coefficient that depends on the fraction of collisions between the aerosol and the air molecules that are considered either specular or diffusive. Values of α typically range from 0.8 to 1.0 for most aerosols, and when no specific experimental information on the partition is available, α is approximated as 0.9. Assuming ideal gas behavior and recognizing that $m_j = M_j / N_{\mathrm{Av}}$ ($N_{\mathrm{Av}} = 6.023 \times 10^{26}$ molecules/kmol), Eq. (6) can be expressed in the form of Eq. (2) as

$$f_{\mathrm{Ep}} = \frac{6\pi\mu d_p [1 + (\alpha\pi/8)]}{9 Kn_p} \tag{7}$$

With $\alpha = 0.9$, the Epstein slip correction factor is simply $C_{\mathrm{Ep}}(Kn_p) = 3.32\ Kn_p$. The linear dependence of C_{Ep} on Kn_p is exact under the assumptions used to derive Eq. (6), which yields results within a few percent or experimental values for near-spherical aerosols with diameters larger than 1 nm (10 Å), and within 10% of experimental values for particles twice as small [13]. For particles comparable in size with small molecules, use of Eq. (7) results in substantially larger errors (≈40–50%). Equation (7) is not applicable to molecules for two main reasons. First, in its derivation, due to its much larger inertia, the velocity of the aerosol is assumed to be small compared to the velocity of the background gas molecules [23,24]. This simplification alone excludes any particle with inertial mass comparable to the molecular mass of the background gas. Second, the quadratic dependence of the friction factor f on d_p (recall that $Kn_p = \ell_j / d_p$) is certainly not applicable to molecules because the effective diameter of a molecule is a very poor proxy for either its inertia or its friction length scale. The empirical coefficients adopted from experimental data for the restitution coefficients used in Eq. (7) refer to aerosols that are roughly uniform in density, and therefore the d_p^2 dependence assumes that the mass of aerosols of different sizes varies with d_p^3. Because of the strong attraction of the positively charged nucleus of heavy gas molecules, the effective electronic cloud diameter of such molecules is only slightly larger than those of the lightest molecules, even though their molecular weights may be tens of times larger. As a relevant example, the lightest spherical molecule, helium, is more than 30 times less massive than the xenon molecule, but is only about 1.5 times smaller in size.

In this work, we show that the replacement of the molecular size by the molecular mass and the simple shape factor discussed above as proxies for the friction length yields a functional form of the slip correction factor that is quite different from the one derived for aerosols by Epstein. The proposed functional form provides unique insight on the effective friction forces acting on molecules, and results in a surprisingly simple estimate for the Schmidt number (and therefore for the binary diffusion coefficient) of simple gases in air. In Sec. III, and before we introduce the new slip correction formulation, we discuss experimental uncertainties and two of the most robust models for comparison. Then, in Sec. IV we discuss the proper dimension of molecules for thermodynamic properties (as opposed to transport properties), and settle on the kinetic diameter as an appropriate measure of size for our purposes. In Sec. V we use scaling arguments to derive the proper functional form of the slip correction factor for molecules, and by doing so we introduce the concepts of molecular Reynolds number Re_{m_i} and no-slip Reynolds number $Re_{j,\mathrm{ns}}$ for the background gas (j = dry air). A comparison with experimental values for spherical molecules (noble gases) confirms our choice of functional form for the slip correction factor, and allows for the determination of the (constant at standard temperature and pressure, STP) no-slip Reynolds number $Re_{j,\mathrm{ns}}$ for dry air. We use the same constant value of $Re_{j,\mathrm{ns}}$ obtained with data for noble gases for the remainder of the comparisons with diatomic and triatomic molecules. Section VI explores the compatibility of the slip correction factor proposed in this work with the CE theory, and offers some recommendation for the estimation of diffusion coefficients for unstable trace gases. Concluding remarks are presented in Sec. VII.

III. Standard Models for Determination of Diffusion Coefficients

Sydney Chapman and David Enskog formalized independently the statistical mechanics approach to diffusion coefficients by considering molecular collisions as nonrigid phenomena that depend on generic attractive and repulsive potentials. The CE theory solves the Boltzmann equation for generic molecular potentials. Results from the CE theory received general acceptance as soon as simple power-law molecular potentials (such as the robust Lennard–Jones 6-12 potential) yielded consistent results for the estimation of viscosity and thermal and binary diffusion coefficient values for a number of simple gases. The entire theory, including several higher-order approximations, is elegantly presented in the monograph by Chapman and Cowling [25]. While obtaining accurate experimental values for the binary diffusion coefficients of gases continues to be a very laborious task [3], the ability to relate results from kinematic viscosity ν and thermal conductivity k measurements to binary diffusion coefficients $\mathcal{D}_{ij}$ allows for the estimation of binary diffusion coefficients for a wide range of gas combinations, even some that are nearly impossible to reproduce experimentally. The result from the CE theory that is most directly relevant to this work is the following [10]:

$$\mathcal{D}_{ij} = \frac{3}{16} \left(2\pi\kappa_B T \frac{M_i + M_j}{M_i M_j} \right)^{1/2} \frac{\tau_{\mathcal{D}}}{n\pi\sigma_{ij}^2 \Omega_{\mathcal{D}}} \tag{8}$$

where n is the number density of molecules in mixture, σ_{ij} is a characteristic length (diameter) for molecular collisions, $\Omega_{\mathcal{D}}$ is a dimensionless collision integral factor, and $\tau_{\mathcal{D}}$ is correction factor of order unity [10]. For molecules dissimilar in size (e.g., He and N_2) $\tau_{\mathcal{D}}$ can be as large as 1.10, but for molecules similar in size it typically ranges from 1.00 to 1.02 only. From the range of possible values for $\tau_{\mathcal{D}}$, it is clear that the CE theory without reference data from experiments is only able to predict binary diffusion coefficients within ≈10% average deviation, regardless of the molecular potential used. Average deviations from experimental values of the order of ≈5–10% have been widely reported [10,26], with the lower deviations indicating fine-tuning of collision parameters, and the upper values indicating predictions of less well-characterized molecules.

The general success of the CE theory also meant that fewer independent experiments was designed or carried out after the theory became widely accepted. To this day, there are very few independent measurements of gas diffusivities that are not based on some aspect of the CE theory. The vast majority of the reported data for gas diffusion is based on gas viscosity measurements [27] that have been translated into binary diffusion coefficients for species i diffusing into species j using the CE theory. Results with the 6-12 Lennard–Jones potential are considered to be accurate to within 8–12% (on average) of the best experimental data available for polar molecules, and generally within 5–8% (also on average) for nonpolar molecules [3]. Deviations from experimental values by as much as 25% are possible, especially for mixtures containing smaller molecules in dilute quantities, or for mixtures involving water vapor [10,26], but such deviations are not common.

As mentioned above, because the CE theory is often used to translate experimental values for binary diffusion coefficients $\mathcal{D}_{ij}$ obtained indirectly from viscosity or thermal conductivity experiments, there are very few data sets that can be considered entirely independent of the CE theory. Marrero and Mason [28] compiled an extensive list of results that, together with the report by Svehla [27] and the earlier compendium by Hirschfelder et al. [26], make up the bulk of the binary diffusion coefficients available in the literature. Other sources that also contain similar information and comparisons include Refs. [10] and [3]. The most reliable data for 22 common gases of interest, polar and nonpolar, compiled from these and a few other more recent sources are summarized in Table 1. The usual procedure is to perform viscosity experiments with a pure gas, and determine, based on CE theory results, the values of the collision length σ_i and maximum energy of attraction e_i that offer the best match with the experiments over a range of temperatures [16]. For the repulsive-attractive Lennard–Jones 6-12 potential

$$\phi(r) = 4e_i\left[\left(\frac{\sigma_i}{r}\right)^{12} - \left(\frac{\sigma_i}{r}\right)^{6}\right] \tag{9}$$

the length scale σ_i is the value of r for which the potential $\phi(r) = 0$.

To convert viscosity measurements into binary coefficients, the same values of σ_i and e_i obtained from viscosity or thermal conductivity experiments are used, although this practice is not always justifiable. The collision integral Ω_μ for viscosity is the same for thermal conductivity [29], but Ω_μ is a slightly larger value than the collision integral $\Omega_\mathcal{D}$ for binary diffusion at a given temperature [30]. Tables for Ω_μ and $\Omega_\mathcal{D}$ as functions of the dimensionless quantity $\kappa_B T/e_{ij}$ are provided in standard references (see, e.g., Refs. [3,16,31]). Table 1 includes, when available, values for the collision diameter σ_i in angstroms, e_i/κ_B in kelvins, and the dimensionless $\kappa_B T/e_{ij}$ and $\Omega_\mathcal{D}$ for 22 gases in air [31]. For consistency, and because there are substantial differences in the values of these quantities published by different authors, we used the value of σ_j as 3.617 Å and e_j/κ_B as 97.0 K for dry air from the updated values provided by Ref. [31], which are themselves based on a modern revision of earlier results published in Ref. [26]. The mixture collision parameters σ_{ij} and e_{ij} are calculated in practice as

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \tag{10}$$

and

$$e_{ij} = \sqrt{e_i e_j} \tag{11}$$

With Eqs. (10) and (11), the binary diffusion coefficient for species i diffusing in species j (dry air) is calculated by the CE theory using the Lennard–Jones 6-12 potential with $\tau_\mathcal{D} = 1$ and assuming ideal gas behavior ($n = 2.504 \times 10^{25}\ \mathrm{m}^{-3}$) as

$$\mathcal{D}_{ij} = \mathcal{A}\frac{\sqrt{T^3(M_i + M_j/M_i M_j)}}{\sigma_{ij}^2 \Omega_\mathcal{D} P}\ \mathrm{m^2/s} \tag{12}$$

where $\mathcal{A}$ is a constant equal to 1.84×10^{-12} in SI units and 1.86×10^{-7} for pressure P in atmospheres and σ_{ij} in angstroms. As shown in Table 1, the collision diameters for most simple gases range from about 2.5 Å to roughly 5 Å, while the collision integral $\Omega_\mathcal{D}$ is a dimensionless quantity of $\mathcal{O}(1)$. Using the same Lennard–Jones 6-12 potential, the CE theory gives the following expression for the dynamic viscosity:

$$\mu_j = \mathcal{B}\frac{\sqrt{M_j T}}{\sigma_j^2 \Omega_\mu}\ \mathrm{kg/ms} \tag{13}$$

where $\mathcal{B}$ is a constant equal to 2.67×10^{-26} in SI units or 2.67×10^{-6} for σ_j in angstroms. Again, assuming ideal gas behavior ($\rho_j = PM_j/\mathcal{R}T$), the kinematic viscosity ν_j is readily obtained from Eq. (13) as

$$\nu_j = \frac{\mathcal{B}\mathcal{R}\sqrt{T^3/M_j}}{\sigma_j^2 \Omega_\mu P}\ \mathrm{m^2/s} \tag{14}$$

and the Schmidt number given by the CE theory $Sc_{i,\mathrm{CE}}$ is simply

$$Sc_{i,\mathrm{CE}} = \frac{\nu_j}{\mathcal{D}_{ij}} = \frac{\mathcal{B}\mathcal{R}}{\mathcal{A}}\frac{\sigma_{ij}^2\Omega_\mathcal{D}}{\sigma_j^2\Omega_\mu}\sqrt{\frac{M_i}{M_i + M_j}} \tag{15}$$

Comparing Sc_i number values (as opposed to $\mathcal{D}_{ij}$) with experiments is preferable for several reasons. Clearly, the explicit effects of pressure and temperature in Eqs. (12) and (13) are eliminated in Eq. (15). Both $\Omega_\mathcal{D}$ and Ω_μ are weak, mildly oscillatory decreasing functions of temperature (see, e.g., Refs. [26,30]) that eventually approach near-constant values of $O(1)$ for high temperatures. Thus, a Lennard–Jones molecule has a slightly smaller cross section at high temperatures when compared to a rigid-sphere model molecule, and the opposite behavior at low temperatures [26], and the combined effect of the viscosity to binary diffusion coefficient ratios in Eq. (15) yields a near-constant value of Sc_i for most species diffusing in air at tropospheric conditions. For these reasons, we select dry air at 300 K

Table 1 Molecular and collision parameters for the Chapman–Enskog theory fitted to experimental data using the Lennard–Jones 6-12 potential

Gas i	Mass	σ_i, Å	$\frac{e_i}{\kappa_B}$, K	$\frac{\kappa_B T^{a}}{e_{ij}}$	$\Omega_\mathcal{D}^{a}$	$\mathcal{D}_{ij}$, $\mathrm{m^2/s}$	$Sc_{i,\mathrm{CE}}$
He	4.003[a]	2.576[a]	10.2[a]	9.54	0.7483	7.18×10^{-5}	0.218
Ne	20.180[a]	2.789[a]	35.7[a]	5.10	0.8398	3.25×10^{-5}	0.481
Ar	39.948[a]	3.432[a]	122.4[a]	2.75	0.9732	1.95×10^{-5}	0.803
Kr	83.798[a]	3.675[a]	170.0[a]	2.34	1.0214	1.53×10^{-5}	1.021
Xe	131.293[a]	4.009[a]	234.7[a]	1.99	1.0770	1.27×10^{-5}	1.236
H_2	2.016[a]	2.915[a]	38.0[a]	4.94	0.8449	7.81×10^{-5}	0.200
OH	17.007[b]	3.147[b]	80[b]	3.41	0.9190	2.81×10^{-5}	0.558
CO	28.010[a]	3.590[a]	110[a]	2.90	0.9588	2.06×10^{-5}	0.761
N_2	28.013[a]	3.667[a]	99.8[a]	3.05	0.9459	2.04×10^{-5}	0.767
NO	30.006[a]	3.470[a]	119[a]	2.79	0.9692	2.07×10^{-5}	0.757
O_2	31.999[a]	3.433[a]	113[a]	2.87	0.9616	2.07×10^{-5}	0.755
HCl	36.458[b]	3.339[b]	345[b]	1.64	1.2672	1.57×10^{-5}	0.998
Cl_2	70.905[a]	4.115[a]	357[a]	1.61	1.1652	1.22×10^{-5}	1.280
HBr	80.908[b]	— —	— —	— —	— —	1.25×10^{-5}	1.253[d]
Br_2	159.808[a]	4.268[a]	520[a]	1.34	1.2572	9.99×10^{-6}	1.568
I_2	253.809[a]	4.982[a]	550[a]	1.30	1.2740	8.05×10^{-6}	1.946
H_2O	18.015[b]	3.737[b]	32[b]	5.38	0.8314	2.58×10^{-5}	0.607
H_2S	34.076[b]	3.623[b]	301[b]	1.76	1.2324	1.51×10^{-5}	1.035
CO_2	44.009[a]	3.996[a]	190[a]	2.21	1.0405	1.53×10^{-5}	1.021
N_2O	44.012[a]	3.879[a]	220[a]	2.05	1.0665	1.54×10^{-5}	1.015
NO_2	46.005[b]	3.765[c]	210.0[c]	2.10	1.0580	1.59×10^{-5}	0.985
SO_2	64.065[a]	4.026[a]	363[a]	1.60	1.1680	1.27×10^{-5}	1.234

The values of Sc_i in air shown in the last column are the most generally accepted values based on fitted CE theory to experiments. Table entries are reproduced with original significant figures from the following sources: [a]Bird et al. [31], [b]Mills and Coimbra [16], [c]Brokaw and Svehla [32], and [d]Tang et al. [6]. With the exception of molecular masses, all last digits on Tables 1 and 2 should be considered speculative (nonsignificant) given the experimental uncertainties and approximations involved. Note that the Sc_i and $\mathcal{D}_{ij}$ values for HBr are not calculated using the CE theory but correspond to the midpoint of the experimental uncertainty range reported by Tang et al. [6]. Slightly different Lennard–Jones parameters have been calculated more recently by Kim and Monroe [33].

as the reference bath for this study, and we make comparisons based on values of the Schmidt number Sc_i for each species. Note that Sc_i is clearly a binary quantity just as $\mathcal{D}_{ij}$. We use the single subscript i in Sc_i instead of Sc_{ij} to mean the Sc number of species i in dry air for simplicity, but also to conform with practice in the heat and mass transfer literature.

In addition to the CE model, a robust method for the estimation of binary diffusion coefficients is the method proposed by Fueller et al. [9] (referred as F in this work). The value of Sc_F is calculated as [9,10]

$$Sc_{i,F} = \frac{\mathcal{F} P \nu_j [(\sum v)_i^{1/3} + (\sum v)_j^{1/3}]^2}{T^{7/4}} \sqrt{\frac{M_i M_j}{M_i + M_j}} \tag{16}$$

where the constant $\mathcal{F}$ is equal to 98.7 in SI units, and equal to 10^7 for P in atmospheres and T in kelvins. Fueller's model relies on experimental determination of the diffusion volume v_i and v_j for simple atoms and molecules. Those values are tabulated, and do not always agree with the original values provided in [9]. In this work we adopt the values presented in [10], which are the most widely cited and are also in agreement with the original values given by [9]. Note that Table 11-1 of [10] also provides values for diffusion-volume increments for C, H, O, N, Cl, and S and (negative increments) for aromatic and heterocyclic rings that can be used to estimate the volumes of molecules that are not included in the main table. Although much simpler to use than the CE theory, Fueller's model also requires the use of tabulated values that are optimized using diffusion data for well-characterized molecules. A perhaps less satisfying feature of the model is that the incremental volumes for atoms do not add up to the total volumes of the molecules, which makes more difficult to combine species reliably based on a limited set volumes for atoms and simple molecules. Nonetheless, the simplicity and robustness of Fueller's method makes it a popular choice for the estimation of diffusion coefficients and Sc numbers. Another important feature of this method is that it makes explicit the fact that diffusion coefficient is, at least to a first approximation, only a function of the molecular mass of the individual species and a combination of molecular length scales (in this case, the cubic roots of the different molecular volumes).

IV. On the Characteristic Size of Molecules

The concept of kinetic diameter as the relevant length scale for the determination of thermodynamic properties of gases was first suggested by [26]. The concept was made popular by Breck's extensive use of it in his monograph on zeolite molecular sieves [34]. The kinetic diameter d_{k_i} of a molecule is defined exactly as σ_i but the value of the length scale for zero potential is calculated by comparison with experimental second virial coefficients for gases at different temperatures [26,35]. The values of d_{k_i} using second virial coefficients may differ slightly from the values of σ_i, which are determined by comparison with either viscosity or thermal conductivity data. For this reason, Hirschfelder et al. [26] recommend the use of the kinetic diameter d_{k_i} for the determination of thermodynamic properties, whereas σ_i should be used for transport properties. More recently, Kim and Monroe [33] showed that higher accuracy calculations of the collision integrals for the Lennard–Jones potentials yield very close values between σ_i and d_{k_i} for spherical (noble gas) molecules.

Mehio et al. [35] developed detailed ab initio quantum mechanics calculations that add strong credibility to the concept of kinetic diameters as a physical representation of the effective size of molecules. In this work we adopt commonly found values for kinetic

Table 2 Kinetic diameters d_{k_i}, molecular Reynolds numbers $\bar{u}_i d_{k_i}/\nu_j$, shape factors χ_i and computed Sc_i using the Chapman–Enskog theory, the proposed model C given by Eq. (24), and Fueller's model F given by Eq. (16) for the 22 molecules listed in Table 1

Gas i	d_{k_i}, Å[ej]	$\bar{u}_i$, m/s	$Re_{m_i} \times 10^3$	χ_i	Sc_i range	$Sc_{i,\mathrm{CE}}$	$Sc_{i,C}$	δ_C, %	$Sc_{i,F}$	δ_F, %
He	2.60	1259.67	10.5	1.00	0.21[h] – 0.23[h]	0.218	0.223	+2	0.233	+7
Ne	2.75	561.03	4.93	1.00	0.47[h] – 0.49[h]	0.481	0.501	+4	0.504	+5
Ar	3.40	398.32	4.33	1.00	0.80[h] – 0.81[h]	0.803	0.705	–12	0.816	+2
Kr	3.60	275.32	3.16	1.00	0.98[h] – 1.10[h]	1.021	1.021	0	1.036	+2
Xe	3.96	219.95	2.78	1.00	1.21[h] – 1.37[abe]	1.236	1.278	+3	1.303	+5
H_2	2.89	1775.02	16.4	1.23	0.20[h] – 0.21[h]	0.200	0.195	–3	0.214	+7
OH	——	611.13	——	1.23	0.56[f] – 0.80[f]	0.558	0.566	+1	0.518	–7
CO	3.76	476.20	5.72	1.23	0.76[a] – 0.76[hi]	0.761	0.726	–5	0.792	+4
N_2	3.64	476.18	5.53	1.23	0.75[h] – 0.78[h]	0.767	0.726	–5	0.778	+1
NO	3.17	460.09	4.66	1.23	0.60[f] – 0.76[h]	0.757	0.751	–1	0.682	–10
O_2	3.46	445.53	4.92	1.23	0.76[h] – 0.79[h]	0.755	0.776	+3	0.784	+4
HCl	3.20	417.40	4.26	1.23	0.91[h] – 1.05[ef]	0.998	0.828	–17	0.880	–12
Cl_2	3.20	299.30	3.06	1.23	1.12[f] – 1.39[f]	1.280	1.155	–10	1.211	–5
HBr	3.50	280.19	3.13	1.23	0.94[f] – 1.76[f]	1.253[d]	1.234	–2	1.207	–4
Br_2	3.50	199.37	2.23	1.23	1.44[f] – 1.73[f]	1.568	1.734	+11	1.650	+5
I_2	——	158.20	——	1.23	1.76[f] – 2.91[f]	1.946	2.185	+12	1.621	–17
H_2O	2.65	593.79	5.02	1.39	0.50[g] – 0.65[g]	0.607	0.658	+8	0.616	+1
H_2S	3.60	431.74	4.96	1.39	1.04[b] – 1.04[i]	1.035	0.905	–13	0.859	–17
CO_2	3.30	379.91	4.00	1.39	1.00[h] – 1.18[h]	1.021	1.028	+1	0.989	–3
N_2O	3.30	379.89	4.00	1.39	1.02[h] – 1.19[h]	1.015	1.028	+1	1.096	+8
NO_2	——	371.57	——	1.39	0.81[f] – 1.69[f]	0.985[c]	1.051	+7	0.935	–5
SO_2	3.60	314.87	3.62	1.39	1.09[f] – 1.44[f]	1.234	1.240	0	1.231	0

Comparing the C and F models against the most widely accepted values obtained by the CE theory, we find that the mean bias deviation is of the same magnitude but slightly smaller for the simple C model [Eq. (24)] at −0.56% versus 1.23% for the F model [Eq. (16)]. The values of δ_C and δ_F are the relative deviations with respect to $Sc_{i,\mathrm{CE}}$. The cumulative relative standard deviation is exactly the same (7.5%) for both C and F models, a value that is compatible with the experimental uncertainty reported by [8] for both the twin tube (TT) and the arrested flow (AF) experimental methods. The ranges of reported values for Sc_i in the sixth column are from the following references: [a]Ref. [31], [b]Ref. [16], [c]Ref. [32], [d]see footnote of Table 1, [e]Ref. [26], [f]Ref. [6], [g]Ref. [37], [h]Ref. [27], [i]Ref. [3], and [j]Ref. [34].

diameters of monoatomic, diatomic, and triatomic molecules in the literature [26,34]. We will show later that the specific choice of kinetic diameter is (at most) of secondary importance in the determination of binary diffusion coefficients and Schmidt numbers. We use kinetic diameters for the determination of the slip correction factor in the next section because the molecular Reynolds number Re_{m_i} is determined by a thermodynamic property ($\bar{u}_i$) of the diffusing gas for a given thermodynamic state of the background gas. Table 2 lists the kinetic diameters d_{k_i} for 19 of the 22 species considered in this work. These are commonly accepted values from standard references [26,34]. Kinetic diameters for OH, I_2, and NO_2 are not reported here because there are discrepancies in the values found in the literature for these molecules. As we shall see, the absence of a few values does not interfere with the analysis and conclusions.

V. Slip Correction Factor for Gas Molecules

To derive a proper functional form of the slip function for small gas molecules, we invoke the concept of correlation path length developed by Taylor [36] for particles and vortices, and applied here to molecules. The correlation path length concept is well known in the aerosol and turbulence research communities [15]:

$$\ell_{\mathrm{cp}} = \sqrt{\bar{u_i^2}} \int_0^\infty R(\tau)\,\mathrm{d}\tau \tag{17}$$

where $R(\tau)$ is the Lagrangian velocity autocorrelation coefficient for the diffusing particle, and τ is the dimensionless time associated with the motion of the particle. The correlation path length ℓ_{cp} is thus the distance for which the motion of the molecule is well-correlated with its status at $\tau = 0$. The diffusion coefficient for a molecule undergoing generic diffusion by continuous movements first proposed by Taylor [36] is given by (see, e.g., [15])

$$\mathcal{D}_{ij} = \bar{u}_i \ell_{\mathrm{cp}} \tag{18}$$

Equating Eq. (18) with Eqs. (1) and (2), the correlation path is given by

$$\ell_{\mathrm{cp}} = \frac{\kappa_B T}{f \bar{u}_i} = \frac{\kappa_B T C(\Pi)}{3\pi\mu d_{k_i} \chi_i \bar{u}_i} \tag{19}$$

Consistent with the discussion above, we seek a functional form for $C(\Pi)$ that renders the correlation path l_{cp} independent of both the diffusion molecule mean velocity and its diameter. In this way, the binary diffusion coefficient in Eq. (18) is composed of two independent parts: one that depends solely on the diffusing gas velocity ($\bar{u}_i$) and another (l_{cp}) that depends on the friction of the background gas j (dry air) and, at most, on the shape (not size) of the diffusing molecule. This is accomplished through straightforward dimensional analysis by setting $C(Re_{m_i}) = Re_{m_i}/Re_{j,\mathrm{ns}}$, where

$$Re_{m_i} = \frac{\bar{u}_i d_{k_i}}{2\nu_j} \tag{20}$$

and $Re_{j,\mathrm{ns}}$ is a reference Reynolds number that depends only on the thermodynamic state of the background gas, and therefore is a constant for given values of temperature and pressure. The molecular correlation path is thus

$$\ell_{\mathrm{cp}} = \frac{\kappa_B T}{6\pi\mu_j \nu_j \chi_i Re_{j,\mathrm{ns}}} \tag{21}$$

Note that while the slip correction factor $C(Re_{m_i})$ depends linearly on the kinetic diameter d_{k_i} of the diffusing molecule, the molecular friction factor

$$f_C = \frac{3\pi\mu_j \nu_j \chi_i Re_{j,\mathrm{ns}}}{\bar{u}_i} \tag{22}$$

is not explicitly dependent on the size (d_{k_i}) of the diffusing molecule i, but rather depends on its shape factor χ_i and its mean velocity $\bar{u}_i = \sqrt{8\mathcal{R}T/\pi M_i}$ (which is uniquely determined by the molecular mass M_i and the temperature of the bath T).

The f_C dependency on d_{k_i} in Eq. (22) is substantially different from the quadratic form derived by Epstein [23] and shown in Eq. (6), but it is consistent with the concept of correlation path length for

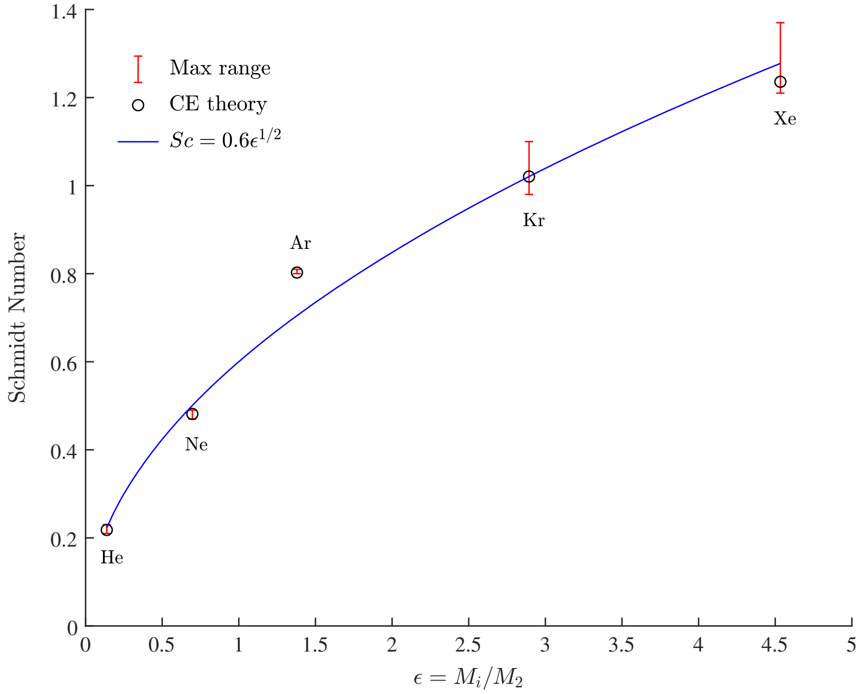

Fig. 1 Schmidt numbers for noble gases i diffusing in dry air j as a function of $\epsilon = M_i/M_2$. Circles correspond to the values calculated using the Chapman–Enkog (CE) theory with the 6-12 Lennard–Jones potential, whereas vertical bars correspond to the maximum range of values reported in standard references (see Sc_i uncertainty ranges in Table 2).

small aerosols. For aerosol particles in air at STP, ℓ_{cp} reaches a minimum of about 7 nm for $d_{p,\min} \approx 200$ nm and grows with $d_p^{1/2}$ for $d_p > d_{p,\min}$ and with $d_p^{-1/2}$ for $d_p < d_{p,\min}$ (see, e.g., Fig. 2.4 of [15]). Equation (21) indicates that, at the molecular level, $\ell_{\mathrm{cp}} \propto d_{k_i}^0$, as the dynamic shape factor χ_i and the molecular velocity $\bar{u}_i$ replace molecular size in the determination of the molecular friction factor.

Once the functional form of the friction factor f_C is known, the Schmidt number $(\nu_j/\mathcal{D}_{ij})$ for gas molecules diffusing in dry air can be readily calculated as

$$Sc_{i,C} = \frac{\nu_j}{\bar{u}_i \ell_{\mathrm{cp}}} = \frac{3N_{\mathrm{Av}}}{\sqrt{2}} \left(\frac{\pi}{\mathcal{R}}\right)^{3/2} \left[\frac{\mu_j \nu_j^2 Re_{j,\mathrm{ns}}}{T^{3/2}}\right] \chi_i \sqrt{M_i} \tag{23}$$

Note that the terms in brackets in Eq. (23) depend only on the properties of the background air and, according to the above interpretation, must be a constant for a given thermodynamic state of the bath. The remarkable feature of Eq. (23) is that it provides a simple way to estimate Sc numbers (and thus binary diffusion coefficients) for any simple molecule based only on the molecular mass and the number of atoms in the molecule, provided that the constant value of $Re_{j,\mathrm{ns}}$ is known for the background gas. It also implies that the Sc numbers of spherical molecules should vary with the square root of the molecular mass. This is confirmed by examining Fig. 1, where the Sc numbers for five spherical molecules (noble gases) are very well fit by the simple expression $Sc_i = 0.11\sqrt{M_i} = 0.60\sqrt{\epsilon}$, where ϵ is the ratio M_i/M_j used here to render the correlation dimensionless.

With $Sc_i/\epsilon^{1/2} = 0.11$ for the noble gas molecules, the value of $Re_{j,\mathrm{ns}}$ for dry air at 300 K and 1 atm is determined from Eq. (23) to be equal to 1.36×10^{-5}, and the slip correction factor is thus simply $C(Re_{m_i}) = 7.35 \times 10^4 Re_{m_i}$. We will use this same constant of proportionality for the remainder of the analysis below.

VI. Results and Discussion

Figure 2 shows that the value of $Re_{j,\mathrm{ns}}$ found by fitting the data to noble gases indeed applies to diatomic ($\chi_2 = 1.23$) and triatomic ($\chi_3 = 1.39$) molecules as well, so that all molecules are very well correlated by

$$Sc_{i,C} = 0.11\chi_i\sqrt{M_i} = 0.60\chi_i\sqrt{\epsilon} \tag{24}$$

which is a remarkably simple expression that can be used to accurately estimate Sc numbers for simple molecules diffusing in air at STP.

The physical interpretation for the no-slip background gas Reynolds number is as follows: $Re_{j,\mathrm{ns}}$ expresses the limiting value of Re_{m_i} for which a slip correction is equal to unity. In other words, the farther away the value of Re_{m_i} for a given molecule is from the constant (much smaller) value of $Re_{j,\mathrm{ns}}$, the higher the slip experienced by the molecule. A hypothetical very dense and slow molecule would experience Stokes drag friction with $C(Re_{m_i}) = 1$, but since such massive molecule does not exist, there is always a need for slip correction for air at STP. Because the main contributor to the value of Re_{m_i} for each molecule is the mean molecular speed $\bar{u}_i$, which is inversely proportional to the square root of its molecular mass M_i, the faster moving, lighter molecules are characterized by higher values of Re_{m_i}, and therefore these molecules experience more slip. This is consistent with the idea of increasing slip for larger values of particle Knudsen numbers from the aerosol theory. Note that the molecular Reynolds number proposed here does not have the same meaning of the usual particle Reynolds number. The former is higher for lighter molecules, which move at higher speeds. The latter is smaller for smaller particles because both the size of the particle and the relative velocity between the particle and the flow are smaller for smaller particles. An important difference between the present approach is that it yields a friction factor f_C that is independent of the size of the molecules, but rather depends on their molecular mass and mean speed. As discussed in the next subsection, this interpretation is entirely compatible with the CE model estimate [Eq. (15)], while dispensing with the need for tabular values.

A. Compatibility with the Chapman–Enskog Theory

Equating $Sc_i = \nu_j f/\kappa_B T$ with Eq. (15), it is possible to derive a functional form for the friction factor f directly from the CE theory using the 6-12 Lennard–Jones potential:

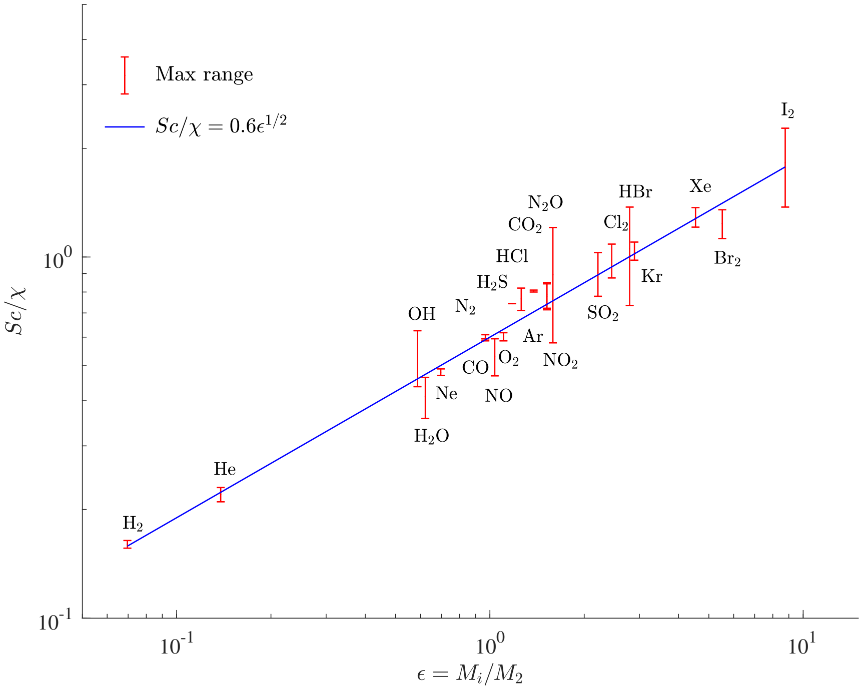

Fig. 2 Ratio of Schmidt number Sc_i and shape factor χ_i as a function of the molecular mass ratio ϵ for all molecules in this study. Note that ϵ varies by more than two orders of magnitude. The values of χ_i are as follows: 1 for monoatomic, 1.23 for diatomic, and 1.39 for triatomic molecules. The range of values (in red) is from the reported spread of data and models listed in Table 2.

$$f_{\mathrm{CE}} = \frac{\kappa_B \Omega_{\mathcal{D}} \sigma_{ij}^2 P}{\mathcal{A} \bar{u}_i} \sqrt{\frac{8\mathcal{R}}{\pi(1+\epsilon)}} \tag{25}$$

Comparing Eq. (25) with Eq. (22) allows us to determine that $Re_{j,\mathrm{ns}}$ must be equal to

$$Re_{j,\mathrm{ns}} = \frac{\kappa_B \Omega_{\mathcal{D}} \sigma_{ij}^2 P}{3\pi \mathcal{A} \mu_j \nu_j \chi_i} \sqrt{\frac{8\mathcal{R}}{\pi(1+\epsilon)}} \tag{26}$$

for both formulations to be equivalent. Furthermore, according to our assumptions, the value of $Re_{j,\mathrm{ns}}$ must be constant for given conditions of temperature and pressure, which implies that the ratio

$$r_{ij} = \frac{\Omega_{\mathcal{D}} \sigma_{ij}^2}{\chi_i \sqrt{1+\epsilon}} \tag{27}$$

must be a constant for all species. Indeed, for σ_{ij} in angstroms, $r_{ij} \approx 7.1$ (with ≈8% relative standard deviation) for all the gases in Tables 1 and 2 (again excluding HBr due to the lack of reliable σ_i and e_i values). Similarly, the quantity

$$\frac{\Omega_{\mathcal{D}} \sigma_{ij}^2}{\chi_i \sqrt{1+\epsilon}} \left[\frac{P \nu_j}{\mathcal{A} T^{3/2}}\right] = \frac{\Omega_{\mathcal{D}} \sigma_{ij}^2}{\Omega_\mu \sigma_j^2 \sqrt{M_i + M_j}} \left[\frac{\mathcal{B}\mathcal{R}}{\chi_i \mathcal{A}}\right] = \frac{Sc_i}{\chi_i \sqrt{M_i}} \approx 0.11$$

is also found to be nearly constant with ≈8% relative standard deviation for all species. Thus, the aerosol-derived theory for the slip correction factor and the simple correlation [Eq. (24)] for Sc_i are fully compatible with the CE theory within the range of uncertainties involved. Note that the value of the no-slip Reynolds number for air at different temperatures and pressures (assuming that the ideal gas behavior holds, and temperatures are well above the critical temperatures for all species involved) can be found from Eq. (23) as

$$Re_{j,\mathrm{ns}} \approx 3.39 \times 10^{-21} \frac{T^{5/2}}{P \nu_j^3} \tag{28}$$

Another way to verify the compatibility of the proposed approach with the CE theory is to plot the proposed slip factor correction $C(Re_{m_i}) = Re_{m_i}/Re_{j,\mathrm{ns}} = 7.35 \times 10^4 Re_{m_i}$ versus the value of the slip correction factor $C(\Pi)$ that returns the CE theory values for Sc_i presented in the last column of Table 1. Figure 3 shows that the proposed slip factor correction is very well correlated for species spanning two orders of magnitude in molecular mass ratio. The agreement in Fig. 3 provides strong support for the slip correction approach and the assumptions made in the previous sections.

Although the agreement with the CE theory is strong, noticeable deviations are observed for some molecules containing hydrogen (H_2O, HCl, H_2S) and for poorly characterized molecules such as Br_2 and I_2. The F method underestimates the value of Sc_i for I_2, whereas the C method barely misses the reported range for Br_2 given by [6]. Such deviations are expected given the simplicity of both approaches. In general, larger deviations from the spherically symmetric Lennard–Jones potential are expected for nonpolar molecules due to the larger values of the approximate angle-independent potential for polar molecules $\delta^* = \zeta^2/e_i\sigma_i^3$, where ζ is the reduced dipole moment for the polar molecule [26]. The small deviation for SO_2 (which has a higher value of δ^* compared with H_2S and HCl) seems to indicate that it is the length of the hydrogen single bond that is somewhat under predicted by the fixed value of $\chi_3 = 1.39$. Both mechanisms seem to contribute to the uncertainty for the molecule with the highest value of δ^* in the table (H_2O). Clearly, instead of using a constant shape factor for all diatomic and another for all triatomic species, one is free to make small adjustments to the aspect ratio χ_i so to take into consideration the length of the bonds, the bent angle, and the size ratio of individual atoms in each molecule. However, the objective of this work is to show that a set of very simple universal rules taken directly from the extensive literature of aerosol theory is able to estimate Sc_i values at least as well as much more complex models, and within the experimental uncertainty of modern techniques.

B. Practical Estimates

Another point worth mentioning is that the smaller, stable molecules that are best characterized experimentally (the ones with small ranges of Sc_i in Table 2) were used to adjust the semi-empirical parameters in both the CE theory and the F model. For this reason, the

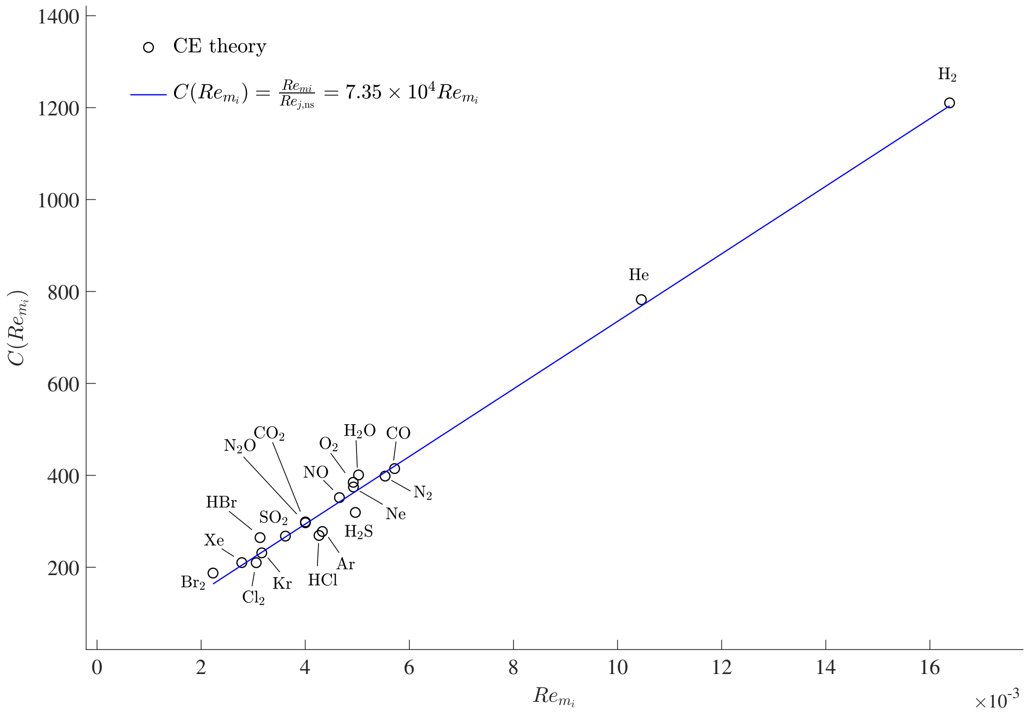

Fig. 3 The slip correction factor $C(\Pi)$ as a function of the molecular Reynolds number Re_{m_i}. The discrete circle values correspond to the values of $C(\Pi)$ in Eqs. (1) and (2) that return the exact values given by the CE theory in Table 1. The high coefficient of determination ($R^2 > 0.99$) in this figure corroborates the choice of the functional form for $C(\Pi) = Re_{m_i}/Re_{j,\mathrm{ns}}$.

CE model is likely to be much closer to experiments for those well-characterized molecules. For unstable trace gases, it is likely that the CE model underpredicts the value of the binary diffusion coefficient by as much as 10% given that the value of $\tau_\mathcal{D}$ in Eq. (12) was taken as unity. Since the binary diffusion coefficient is underpredicted, the values of Sc_i for poorly studied molecules are likely to be overpredicted by ≈10%.

Massman [12] argued that the incorrect use of Graham's law led some researchers to estimate the binary diffusion coefficient of ozone in air from the (still poorly characterized) binary coefficient of water vapor in air using the inverse square root of the respective molecular masses. We showed here that this approximation is not only compatible with the CE theory, but is actually enforced by it, as long as the molecules have the same number of atoms. Both H_2O and O_3 are bent molecules, but while H_2O has two single hydrogen bonds, O_3 has one double and one single bond. Potential minor adjustments to account for the different bonds make the ratio not quite exact, but the strong agreement found in this work with no adjustments to the values of χ_i indicates that using the square root ratio is a very good approximation and within experimental uncertainty. The recent measurements by [8] place the value of Sc_{O_3} in air at 300 K and 1 atm at 0.868, with the highest experimental value at 0.935 and the lowest at 0.810. This is substantially lower than the CE theory estimate of 1.016 reported by Massman [12]. Massman [12] estimated Sc_{O_3} as 0.951, about 7% lower than his own CE theory estimate. Equation (24) with coefficient 0.11 yields a value of 1.059, which is compatible with the CE theory value given by [12]. According to the above discussion, if the coefficient in Eq. (24) is reduced to 0.10 given that ozone is not a molecule that has entered the experimentally adjusted database, the model proposed here yields $Sc_{O_3} = 0.963$, which is still 3% higher than the range of measured values given by [8]. Interestingly, estimating Sc_{O_3} from the value of another bent molecule (SO_2, which is better characterized than H_2O) as $\sqrt{M_{O_3}/M_{SO_2}} \times Sc_{SO_2}$ yields $Sc_{O_3} = 0.929$, a value that is compatible with the experiments of [8] and the earlier estimate by [12].

VII. Conclusions

This work advances our understanding of gaseous diffusion air in many different ways. First, it summarizes both classical and recent experimental results for polar and nonpolar molecules and for stable and unstable trace gases that are important for a large number of atmospheric processes on Earth.

Second, it shows that the rigorous results obtained for small aerosols diffusing in the free molecule flow regime can be extended to molecular scales as long as the proper friction coefficients are used. The choice of the functional form for the slip correction coefficient used in this work is not only compatible, but also strongly supported by the CE theory, which approaches the molecular diffusion problem from Boltzmann statistics. The extension of the Stokes–Einstein–Taylor theory to molecular levels with substantial slip contributed in this work is entirely novel. Comparison with experimental results at STP conditions shows that molecules in this regime behave statistically as small aerosols, which is likely to result in new physical insights given the extensive results for aerosol diffusion in different flow configurations.

Third, the arguments used to derive Eq. (23) result in a very simple correlation, Eq. (24), which reproduces Schmidt numbers and binary diffusion coefficients within the general uncertainty of much more complex models, and also within the experimental uncertainty of modern experimental techniques. The proposed correlation relies on a simple rule that links the aspect ratio of molecules to the number of atoms in the molecule, dispensing with the need for molecular volumes or collision length scales. Diffusion coefficients for simple molecules (with molecular mass M_i) in dry atmospheric air (with molecular mass M_j) can be readily evaluated at the reference temperature of 300 K as

$$\mathcal{D}_{ij}(300\ \mathrm{K}) = \frac{\nu_j}{0.6\chi_i\sqrt{M_i/M_j}} \tag{29}$$

where ν_j is the viscosity of air at 300 K, and χ_i is 1.00 for monoatomic, 1.23 for diatomic, and 1.39 for triatomic molecules. As shown in Table 2, use of Eq. (29) yields results at least as good as the semi-empirical model by Fueller et al. [9], which is used broadly in the literature but requires tabulated values for the volume of different atoms and molecules.

Once the diffusion coefficient is estimated at 300 K, it can be translated to other bath temperatures by using the well-known conversion relations derived from Eq. (12), or simpler (but more accurate) semi-empirical relations such as

$$\mathcal{D}_{ij}(T) = \mathcal{D}_{ij}(300\ \mathrm{K})(T/300\ \mathrm{K})^b \tag{30}$$

Many authors in both the atmospheric physics and the aerospace engineering communities use different values of b for air (typically between 1.50 and 1.85) depending on the temperature range under study and the reference temperature used. For most applications in air, the b exponent can be taken as 1.75 (see, e.g., [6]) as per Fueller's semi-empirical method [Eq. (16)], or adjusted to experimental values when those are available. For example, Langerberg et al. [8] recommends a b value of 1.83 for ozone diffusing in air for a reference temperature of 273 K. Similarly, a b exponent of 1.685 is recommended by Marrero and Mason [28] for H_2O in air for a reference temperature of 256 K. The CE theory predicts a value of $b \sim 1.5 + \delta$ [see Eq. (12)] with positive δ deviations arising from the $\Omega_\mathcal{D}$ term as this value changes with temperature more strongly at low temperatures ($\Omega_\mathcal{D} \sim \kappa_B T/e_{ij}^{-0.44}$ for $\kappa_B T/e_{ij} < 4$) and becomes almost constant at high temperatures ($\Omega_\mathcal{D} \sim \kappa_B T/e_{ij}^{-0.17}$ for $\kappa_B T/e_{ij} > 4$). This behavior implies a value of b given by the CE theory ranging from 1.67 to 1.94. Just as with the CE theory, the slip-correction theory proposed here predicts that the Sc number must be nearly independent of temperature, which means that the temperature dependence of the binary diffusion coefficient must follow the behavior of the kinematic viscosity. Equation (28) shows that the nonslip background flow Reynolds number varies inversely with pressure and with the 5/2 power on temperature, as well as with the inverse cubic power of the kinematic viscosity of the bath gas. Equation (28) combined with Eqs. (1) and (22) yield a friction factor f_C that varies with T/ν_j, and a binary diffusion coefficients in air varying directly with ν_j, as expected. The kinematic viscosity of air for temperatures between 250 and 400 K can be well approximated by the simple power-law behavior $\nu_{\mathrm{air}} \sim 9.6 \times 10^{-10} T^{1.7}\ \mathrm{m^2/s}$, which implies a value of $b \sim 1.7$. If the temperature is not too far removed from 300 K, all these slightly different values of b yield binary diffusion coefficients that are acceptable for most practical applications. Finally, Eq. (28) and the procedure outlined in Sec. V can be used to estimate the no-slip molecular Reynolds numbers for other background gases such as Ne, Ar, N_2, O_2, and CO_2 with similar accuracy as reported in this work (see additional tables in the supplemental materials S1; or go to the Supplemental Materials link that accompanies the electronic version of this paper at http://arc.aiaa.org).

The fact that the number of atoms in a molecule is shown in this work to be a good proxy for the molecular aspect ratio can be explained by the following argument: due to the strong attraction of heavy nuclei, the electron clouds of most atoms are of comparable size, with the exception of the smallest atoms of hydrogen and helium. However, helium is inert, and the longer, single bonds of hydrogen tend to offset its smaller size. This argument is straightforward for diatomic and colinear triatomic molecules (e.g., carbon dioxide). For bent triatomic molecules the argument is less obvious, but the good agreement found using a constant value of χ_3 for four triatomic molecules that do not contain hydrogen bonds gives support to the overall approach (see the excellent agreement shown in Fig. 3).

Finally, it is entirely possible that very simple rules distinguishing covalent and ionic bonds or colinear and bent molecules could be developed to improve the agreement between the proposed correlation, Eq. (24), and experimental values. However, the simplicity of the model proposed here and its ability to reproduce molecular behavior based on molecular masses and shape factors only are intellectually satisfying and of great practical relevance in both science and in engineering applications.

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