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Dynamic Shape Factors for Binary Diffusion of Organic Compounds in Air

A thesis submitted in partial satisfaction of the
requirements for the degree Master of Science

in

Engineering Sciences (Mechanical Engineering)

by

Nathan H. Lubega

Committee in charge:

Professor Carlos F.M. Coimbra, Chair
Professor Renkun Chen
Professor Kalyanasundaram Seshadri

2021

The thesis of Nathan H. Lubega is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego

2021

DEDICATION

I dedicate this thesis work to my family and many friends. A special feeling of gratitude to my grandmother, Alice Lubega who raised me and always believed in me.

I also dedicate this thesis to my many friends who have supported me through-out the process. I will always appreciate all they have done, especially the black-grads at UC San Diego for providing support when things got rough and lifting me up I was down.

EPIGRAPH

Education is the most powerful weapon which you can use to change the world.

Nelson Mandela

TABLE OF CONTENTS

Thesis Approval Page	iii
Dedication	iv
Epigraph	v
Table of Contents	vi
List of Figures	vii
List of Tables	viii
Preface	ix
Acknowledgements	x
Abstract of the Thesis	xi
Introduction	1
Chapter 1 Background	4
1.1 Chapman-Enskog theory	4
1.2 Fuller Method	7
Chapter 2 Aerosol Theory	10
2.1 Brownian Motion	10
2.2 Slip Correction Factor	11
Chapter 3 Methods	14
3.1 Bonding Configurations	14
3.2 Quantitative Analysis	16
Chapter 4 Results	17
4.1 Dynamic Shape Factor	17
4.2 Binary Diffusion Coefficients	18
Chapter 5 Discussion	20
5.1 Slip Correction for Organic Molecules	20
5.2 Model Validity	21
Chapter 6 Conclusion	25
Bibliography	27

LIST OF FIGURES

Figure 0.1.	Global, annual mean radiative forcings (Wm^2) from pre-industrial (1750) to present. A vertical line without a rectangular bar and with “o” delimiters denotes a forcing for which no central estimate can be given owing to large uncertainties. A “level of scientific understanding” (LOSU) index is accorded to each forcing, with H, M, L and VL denoting high, medium, low and very low levels, respectively (Forster et al., 2007)	2
Figure 1.1.	A molecule collision showing the collision diameter, d and the collision cross sectional area (dotted region) equal to $\sigma_c = \pi d^2$ (Serway and Jewett, 2018)	5
Figure 2.1.	Brownian motion of a spherical particle suspended in a medium showing the random-walk path as it collides with other molecules in the medium (Friedlander et al., 2000).	10
Figure 3.1.	Bonding configurations of carbon as predicted by the Valence-Shell Electron-Pair Repulsion (VSEPR) theory, including bonding partners and corresponding angles (Reusch, 2013).	15
Figure 5.1.	The slip correction factor $C(\cdot)$ as a function of the molecular Reynolds number Re_{m_i} . The circle values correspond to the values of $C(\cdot)$ in Equations (1) and (2) that return the exact values given by the CE theory in Table I. The high coefficient of determination ($R^2 > 0.99$) in this figure corroborates the choice of the functional form for $C(\cdot) = Re_{m_i}/Re_{j,ns}$, as well as the use of kinetic diameters d_{k_i} as the proper molecular length scale in Re_{m_i}	21
Figure 5.2.	Schmidt numbers as a function of molecular weight for different groups of organic compounds diffusing in dry air under normal conditions $T = 298$ [K] and $P = 1$ atm. Circles show values calculated with the Chapman-Enskog (CE) theory with the 6-12 Lennard-Jones potential, triangles are determined with the semi-empirical Fuller (F) method, crosses denote those determined using the power law expression presented combined with the Coimbra (C) aerosol theory, and vertical bars correspond to the range of values reported in experimental results	22

LIST OF TABLES

Table 1.1.	Molecular and collision parameters for the first 8 normal linear hydrocarbons and primary alcohols determined by applying the Chapman-Enskog (CE) theory fitted to experimental data at $T = 298$ [K] and $P = 1$ atm using the Lennard-Jones 6-12 potential. The values of $Sc_{i,CE}$ in air shown in the last column are the most generally accepted values based on fitted CE theory to experiments. With the exception of molecular masses, all last digits on the tables provided should be considered speculative (non-significant) given the experimental uncertainties and approximations involved.	6
Table 1.2.	Atomic Diffusion Volumes for Determining Binary Diffusion Coefficients as listed in Table 11-1 of Reid et. al [1967]	8
Table 4.1.	Coefficients for Determining Dynamic Shape Factors χ_i for Calculating Binary Diffusion Coefficients in Organic Compounds Diffusing in Air at Normal Conditions	17
Table 4.2.	Coefficients for determining binary diffusion coefficients Sc_i and D_{ij} for organic compounds diffusing in dry air at normal conditions $T=298$ [K] and $P=1$ atm	18
Table 5.1.	Shape factors χ_i calculated from the proposed correlation and computed Sc_i comparison with the Chapman-Enskog (CE) theory, Coimbra's model (C), and Fuller's model (F) for the molecules listed in Table I. Comparing the C and F model,s and most widely accepted values obtained by the CE theory against the experimental results (EXP), we find that the mean bias deviation is . The values of Δ_{CE} , Δ_C and Δ_F are the relative deviations with respect to $Sc_{i,EXP}$	24

PREFACE

Before you lies the thesis “Dynamic Shape Factors of Binary Diffusion of Organic Compounds in Air”. It has been written to fulfill the graduation requirements of the Engineering Sciences (Mechanical Engineering) at UC San Diego. I was engaged in researching and writing this thesis from September 2019 to June 2021.

ACKNOWLEDGEMENTS

First, I wish to thank my thesis committee. Without their guidance, I would not have made it. Professor Renkun Chen, and Professor Kalyanasundaram Seshadri served as committee members, and Professor Carlos Coimbra, my Chair, went above and beyond to help me reach my goal.

I would also like to acknowledge the “Coimbra lab” without whom my research would not be possible. It is their support that helped me in an immeasurable way.

Chapter 4, is currently being prepared for submission for publication of the material. Dynamic Shape Factors for Binary Diffusion of Organic Compounds in Air 2021. Lubega, Nathan H; Nguyen, Anthony; Coimbra, Carlos F.M. The thesis author was the primary investigator and author of this material.

ABSTRACT OF THE THESIS

Dynamic Shape Factors for Binary Diffusion of Organic Compounds in Air

by

Nathan H. Lubega

Master of Science in Engineering Sciences (Mechanical Engineering)

University of California San Diego, 2021

Professor Carlos F.M. Coimbra, Chair

This work determines the dynamic shape factor for organic compounds diffusing in dry air at normal conditions $T=298$ [K] and $P=1$ atm. Aerosol theory is used to adapt the functional form of the slip correction factor $C(\cdot)$ as a function of the molecular Reynolds number $Re_{m,i}$ such that $C(Re_{m,i}) = 7.35 \times 10^4 Re_{m,i}$. A simple power law expression is then developed of the form $\chi_i = c_1 \cdot n^{c_2}$ and coefficients are found by fitting existing experimental and numerical data. These results are compared to widely used semi-empirical techniques to show their accuracy in determining binary diffusion coefficients with a mean deviation of $\pm 4\%$ for organic compounds diffusing in air at normal conditions.

Introduction

The radiative balance in the atmosphere is strongly influenced by atmospheric aerosols that scatter and absorb solar radiation. Smaller aerosols closer in size to wavelengths in the visible region can have a delocalized impact on climate and the environment as they are transported far from their emission regions by physical processes such as advection, convection, and diffusion (Jimenez et al., 2009). Sub-micron organic aerosols have significant effects on global climate, visibility, human health, and ecological integrity. These organic aerosol particles can be produced by condensation of semi- and low-volatility organic vapors which are directly emitted or formed by gas phase reactions between atmospheric oxidants and volatile organic compounds of biogenic and anthropogenic precursors with the most notable being methane in our atmosphere (Tang et al., 2015).

Organic aerosols affect climate by scattering and adsorbing solar and terrestrial radiation, modifying cloud properties by acting as cloud condensation nuclei (CCN), and play an important role in direct and indirect aerosol forcing. These organic aerosols (OA) contribute as high as 90% of the the total sub-micron particulate mass fraction of fine aerosols in tropical forested areas and $\sim 20 - 50\%$ at continental mid-latitudes (Kanakidou et al., 2005). These organic components are grouped into primary organic aerosols (POA), that are emitted directly into the atmosphere by fossil fuel combustion, biomass burning, and other sources, and secondary organic aerosols (SOA), that are formed by condensation of semi- and low-volatility organic compounds transferring from gas-phase to aerosol in the atmosphere.

The characterization of these organic species in climate simulations has so far been unable to accurately predict the mass fraction of OA and in some cases underestimated the

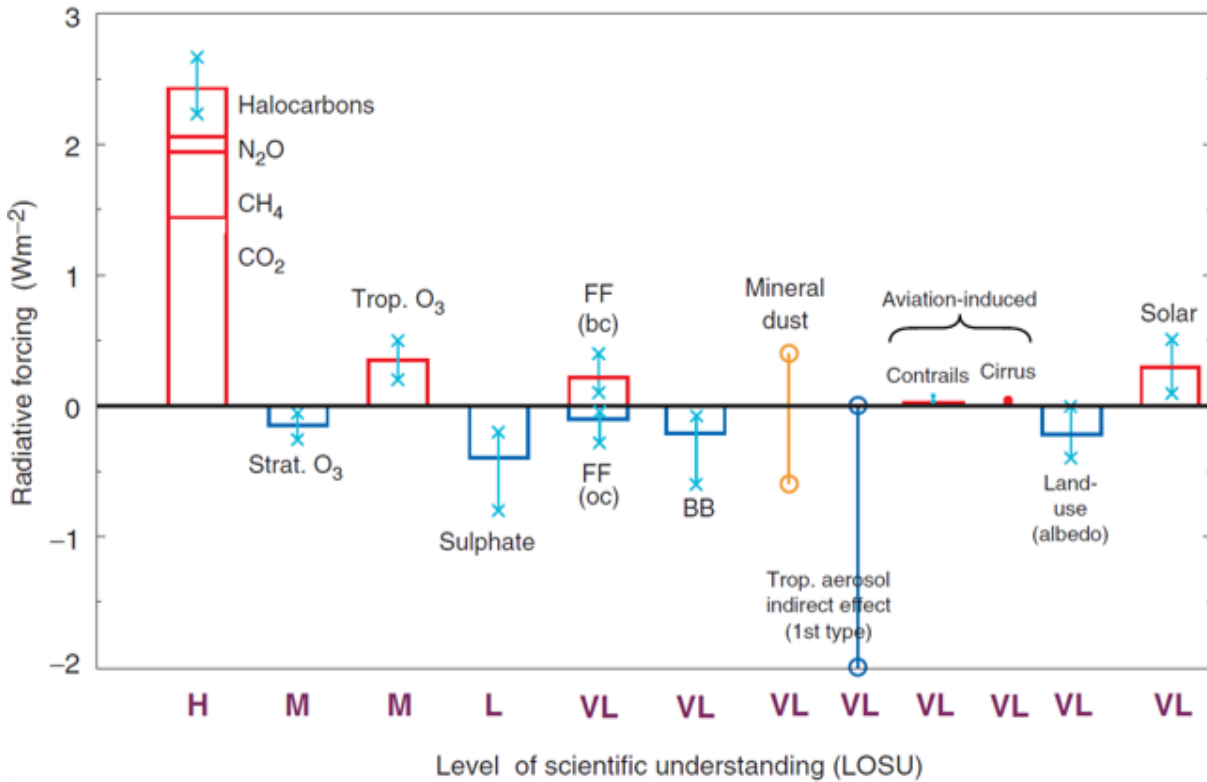


Figure 0.1. Global, annual mean radiative forcings (Wm^{-2}) from pre-industrial (1750) to present. A vertical line without a rectangular bar and with “o” delimiters denotes a forcing for which no central estimate can be given owing to large uncertainties. A “level of scientific understanding” (LOSU) index is accorded to each forcing, with H, M, L and VL denoting high, medium, low and very low levels, respectively (Forster et al., 2007)

concentration by an order of magnitude or more, and explicit modeling can be too complex for larger-scale simulations (Johnson et al., 2006; Zhang et al., 2007). Fig (0.1) above shows the level of scientific understanding for these processes in the atmosphere. The relative uncertainty of diffusing constants is a source of frustration given the importance of diffusion of suspended organic aerosols in the atmosphere and the difficulty in measuring by conventional methods. And while well-established models and experimental techniques exist, it is only for a few well-characterized stable molecules which when compared to experimental values by Tang et al. (2015), the reported agreement is $\pm 30\%$. Therefore, a better understanding of gas-phase reactions and their physical processes is required to work to improve air quality (Docherty et al., 2008) and reduce the uncertainties and complexities of simulating these OA compounds in global

climate models.

The objectives of this work are to; (1) determine if the slip correction factor relation developed for simple gases by Coimbra et al. (2021) can be extended to organic compounds, (2) propose a simple correlation to determine the dynamic shape factors of organic compounds diffusing in air at normal conditions, and (3) compare the results of the binary diffusion coefficients developed by these dynamic shape factors with the commonly used and most reliable semi-empirical models quantify the accuracy of these results.

Chapter 1

Background

The most commonly accepted techniques for determining binary diffusion coefficients of a binary gas-phase mixture are introduced below. These are the Chapman-Enskog theory and the Fuller method.

1.1 Chapman-Enskog theory

The most widely accepted method of calculating binary diffusion constants is the Chapman-Enskog mathematical theory of nonuniform gases formalized by Chapman and Cowling (1990) referred to as (CE) in this paper. This method considers the forces acting between a pair of molecules during a collision and characterizes them by a potential energy of interaction ϕ which is empirically represented using the Lennard-Jones 6-12 potential shown below (Mills and Coimbra, 2016).

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1.1)$$

where ϵ is the maximum energy of attraction between the pair of molecules and σ , the collision diameter is shown in Figure (1.1) and is determined as the value of r for which $\phi(r) = 0$.

In this work, Lennard-Jones collision diameters σ in angstroms, and their corresponding potential-energy of attraction ϵ are calculated respectively with the correlations by Bird et al. (2006) using the critical temperature T_c , and pressure P_c with critical point data obtained from

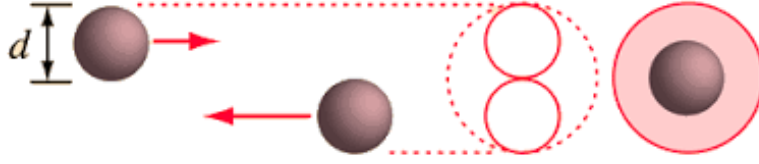


Figure 1.1. A molecule collision showing the collision diameter, d and the collision cross sectional area (dotted region) equal to $\sigma_c = \pi d^2$ (Serway and Jewett, 2018)

Yaws (2014), Lide (2004), and Linstrom and Mallard.

$$\sigma = 2.44 \left(\frac{T_c}{P_c} \right)^{1/3} \quad (1.2)$$

$$\varepsilon/k_B = 0.77T_c \quad (1.3)$$

For a binary system, the empirical relation below is used where i and j denote the diffusing organic compound and background gas (air) respectively. Therefore the mixture collision parameters, σ_{ij} and ε_{ij} are calculated as

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (1.4)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (1.5)$$

The dimensionless collision integrals for viscosity Ω_μ and mass diffusivity Ω_D are weakly dependent on temperature and are well tabulated in standard references. However, for the purpose of this work, they have been calculated using the following curve-fits by Neufeld et al. (1972) where T^* is the reduced temperature given by $T^* = k_B T / \varepsilon$ and k_B is the Boltzmann constant equal to 1.38×10^{-23} J/K.

$$\Omega_\mu = \frac{1.161}{T^{*0.149}} + \frac{0.525}{\exp(0.773T^*)} + \frac{2.162}{\exp(2.438T^*)} \quad (1.6)$$

Table 1.1. Molecular and collision parameters for the first 8 normal linear hydrocarbons and primary alcohols determined by applying the Chapman-Enskog (CE) theory fitted to experimental data at $T = 298$ [K] and $P = 1$ atm using the Lennard-Jones 6-12 potential. The values of $Sc_{i,CE}$ in air shown in the last column are the most generally accepted values based on fitted CE theory to experiments. With the exception of molecular masses, all last digits on the tables provided should be considered speculative (non-significant) given the experimental uncertainties and approximations involved.

Gas i	Symbol	Mass	$\sigma_i[\text{\AA}]$	$\varepsilon/k_B[\text{K}]$	$k_B T/\varepsilon$	Ω_μ	Ω_D	$D_{ij}[\text{m}^2/\text{s}]$	$Sc_{i,CE}$
methane	CH ₄	16.04	3.936	146.7	2.437	1.170	1.008	2.02×10^{-5}	0.767
ethane	C ₂ H ₆	30.07	4.518	235.1	1.925	1.417	1.090	1.35×10^{-5}	1.148
propane	C ₃ H ₈	44.10	5.042	284.8	1.749	1.556	1.129	1.06×10^{-5}	1.464
n-butane	C ₄ H ₁₀	58.12	5.483	327.3	1.631	1.672	1.160	8.88×10^{-6}	1.745
n-pentane	C ₅ H ₁₂	72.15	5.898	361.7	1.552	1.763	1.183	7.71×10^{-6}	2.011
n-hexane	C ₆ H ₁₄	86.18	6.274	390.9	1.493	1.837	1.202	6.86×10^{-6}	2.259
n-heptane	C ₇ H ₁₆	100.20	6.621	416.0	1.447	1.900	1.217	6.21×10^{-6}	2.494
n-octane	C ₈ H ₁₈	114.23	6.953	437.9	1.411	1.951	1.230	5.69×10^{-6}	2.724
ethene	C ₂ H ₄	28.05	4.352	217.4	2.002	1.367	1.075	1.45×10^{-5}	1.069
propene	C ₃ H ₆	42.08	4.888	280.1	1.761	1.545	1.126	1.11×10^{-5}	1.397
1-butene	C ₄ H ₈	56.10	5.355	323.0	1.642	1.661	1.157	9.21×10^{-6}	1.683
1-pentene	C ₅ H ₁₀	70.13	5.771	375.9	1.560	1.753	1.180	7.97×10^{-6}	1.945
1-hexene	C ₆ H ₁₂	84.15	6.137	388.1	1.498	1.830	1.200	7.08×10^{-6}	2.187
1-heptene	C ₇ H ₁₄	98.18	6.470	413.7	1.451	1.894	1.216	6.42×10^{-6}	2.414
1-octene	C ₈ H ₁₆	112.20	6.778	436.6	1.414	1.948	1.230	5.90×10^{-6}	2.629
ethyne	C ₂ H ₂	26.04	4.197	237.4	1.916	1.423	1.092	1.51×10^{-5}	1.024
propyne	C ₃ H ₄	40.06	4.721	309.8	1.677	1.625	1.147	1.14×10^{-5}	1.354
1-butyne	C ₄ H ₆	54.09	5.202	338.8	1.604	1.703	1.167	9.50×10^{-6}	1.631
1-pentyne	C ₅ H ₈	68.12	5.638	379.9	1.514	1.810	1.195	8.13×10^{-6}	1.906
1-hexyne	C ₆ H ₁₀	82.14	5.953	415.3	1.448	1.897	1.217	7.28×10^{-6}	2.130
1-heptyne	C ₇ H ₁₂	96.17	6.399	430.4	1.423	1.934	1.226	6.47×10^{-6}	2.394
1-octyne	C ₈ H ₁₄	110.20	6.574	460.8	1.375	2.004	1.244	6.07×10^{-6}	2.552
methanol	CH ₄ O	32.04	4.536	394.6	1.486	1.847	1.204	1.20×10^{-5}	1.293
ethanol	C ₂ H ₆ O	46.07	4.977	395.8	1.484	1.850	1.205	9.98×10^{-6}	1.553
1-propanol	C ₃ H ₈ O	60.10	5.347	413.3	1.452	1.893	1.216	8.68×10^{-6}	1.786
1-butanol	C ₄ H ₁₀ O	74.12	5.726	433.5	1.418	1.941	1.228	7.67×10^{-6}	2.021
1-pentanol	C ₅ H ₁₂ O	88.15	6.056	452.8	1.387	1.986	1.239	6.93×10^{-6}	2.235
1-hexanol	C ₆ H ₁₄ O	102.18	6.406	469.9	1.362	2.025	1.249	6.30×10^{-6}	2.460
1-heptanol	C ₇ H ₁₆ O	116.20	6.728	487.1	1.337	2.063	1.259	5.79×10^{-6}	2.675
1-octanol	C ₈ H ₁₈ O	130.23	6.995	501.3	1.318	2.093	1.267	5.41×10^{-6}	2.862

$$\Omega_D = \frac{1.060}{T^{*0.156}} + \frac{0.193}{\exp(0.476T^*)} + \frac{1.036}{\exp(1.530T^*)} + \frac{1.765}{\exp(3.894T^*)} \quad (1.7)$$

Therefore the diffusion constant for a binary system is can be determined as follows

$$D_{ij} = \mathcal{A} \frac{\sqrt{T^3 \left(\frac{M_i + M_j}{M_i M_j} \right)}}{\sigma_{ij}^2 \Omega_D P} \quad (1.8)$$

where D_{ij} is the binary diffusion coefficient in [m²/s], \mathcal{A} is a proportionality constant equal to 1.84×10^{-12} in SI units and 1.86×10^{-7} for temperature T in kelvins, pressure P in atmospheres, σ_{ij} is the collision diameter in angstroms, and M denotes the molecular mass of the diffusing species i and j respectively. Following $Sc_i = \nu_j / D_{ij}$, where ν_j is the kinematic viscosity of the bulk gas, the Schmidt number is then defined below.

$$Sc_{i,CE} = \frac{\mathcal{B}R \sigma_{ij}^2 \Omega_D}{\mathcal{A} \sigma_j^2 \Omega_\mu} \sqrt{\frac{M_i}{M_i + M_j}} \quad (1.9)$$

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 and the universal gas constant R, 8314.5 J/kmol K. The values for the organic molecules used for comparison in this work have been tabulated in Table 1.1 above and independently verified from published values Marrero and Mason (1972); Wang and Frenklach (1994); Bartlett et al. (1968).

1.2 Fuller Method

Another commonly referenced and robust technique to calculate binary diffusion coefficients is the semi-empirical method developed by Fuller et al. (1966). The Fuller method, denoted as (F) in this work, sums empirically determined atomic diffusion-volume increments to estimate the total volume of the gas molecule. The most widely accepted values of the diffusion volumes that are used in this work, and are in agreement with those originally proposed by Fuller et al. (1966) are adopted from table 11-1 of Reid et al. (1987) and shown below.

The binary diffusion constant D_{ij} as defined by the least squares correlation developed by Fuller et al. (1966) is as follows.

$$D_{ij} = \frac{T^{7/4} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}}{\mathcal{F} P [(\sum v)_i^{1/3} + (\sum v)_j^{1/3}]^2} \quad (1.10)$$

where v represents the atomic diffusion volume for each gas in the mixture, the constant \mathcal{F} is equal to 9.87×10^{-3} in SI units, and equal to 10^3 for P in atmospheres and T in Kelvins.

Table 1.2. Atomic Diffusion Volumes for Determining Binary Diffusion Coefficients as listed in Table 11-1 of Reid et. al [1967]

Atomic and Structural Diffusion Volume Increments			
C	15.9	F	14.7
H	2.31	Cl	21.0
O	6.11	Br	21.9
N	4.54	I	29.8
Aromatic ring	-18.3	S	22.9
Hetrocyclic ring	-18.3		
Diffusion Volumes of Simple Molecules			
He	2.67	CO	18.0
Ne	5.98	CO ₂	26.9
Ar	16.2	N ₂ O	35.9
Kr	24.5	NH ₃	20.7
Xe	32.7	H ₂ O	13.1
H ₂	6.12	SF ₆	71.3
D ₂	6.84	Cl ₂	38.4
N ₂	18.5	Br ₂	69.0
O ₂	16.3	SO ₂	41.8
Air	19.7		

Similarly, the Schmidt number is determined using $Sc_i = v_j/D_{ij}$ and calculated using the equation below.

$$Sc_{i,F} = \mathcal{F} P v_j \frac{[(\sum v)_i^{1/3} + (\sum v)_j^{1/3}]^2}{T^{7/4} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}} \quad (1.11)$$

It is clear that this method provides a much needed simplicity for estimating binary

diffusion coefficients and the associated Schmidt numbers compare to the CE theory above. However, a major point of note for this model is that incremental atomic volumes do not always add up to the total volumes of the molecules. This makes it difficult to combine species reliably based on the limited number of molecular volumes provided and proves to introduce a large uncertainty when determining binary diffusion coefficients of longer less-characterized molecules such as those found in the organic compounds we are interested in. As we will show later, this tends to underestimate the Schmidt numbers of longer molecules calculated with this method.

Chapter 2

Aerosol Theory

In order to develop a simple and more robust method as compared to the CE theory and Fuller method presented previously, we look to aerosol theory to determine binary diffusion coefficients and Schmidt numbers of organic molecules diffusing in dry air.

2.1 Brownian Motion

The theory behind diffusion of aerosols is based on the Brownian motion of a spherical particle suspended in a medium as shown in Figure (5.2) below, and relates it to the molecular motion of gas molecules using the Stokes-Einstein relation Fuchs et al. (1964).

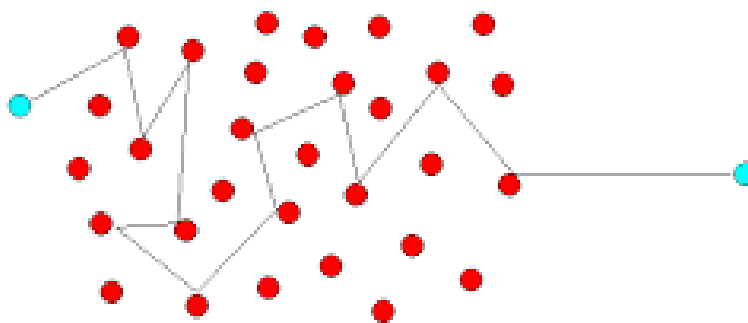


Figure 2.1. Brownian motion of a spherical particle suspended in a medium showing the random-walk path as it collides with other molecules in the medium (Friedlander et al., 2000).

Brownian diffusion of a particle can be expressed through the Stokes-Einstein relation which provides a relationship between the coefficient of diffusion to the properties of the fluid

and the particle through the friction coefficient.

$$D_p = \frac{k_B T}{f} \quad (2.1)$$

for the Stokes friction coefficient f given by

$$f = \frac{3\pi\mu_j d_p \chi_p}{C(\cdot)} \quad (2.2)$$

where d_p is the effective diameter of the diffusing particle, μ_j is the dynamic viscosity of the bulk gas, $C(\cdot)$ is the slip correction factor, and χ_p is the shape factor for non-spherical aerosols for which this work will propose a solution for organic compounds.

2.2 Slip Correction Factor

The slip correction factor $C(\cdot)$, introduced as a correction to the Stokes friction coefficient, is a function of the Knudsen number $Kn_p = \ell_j/d_p$ where the ℓ_j is the mean free path of the background gas molecules given by the following Knudsen and Weber (1911);

$$\ell_j = v_j \left(\frac{\pi M_j}{2RT} \right)^{1/2} \quad (2.3)$$

Thus the slip correction factor can be calculated using the correlation proposed by Cunningham (1910) as

$$C(Kn_p) = 1 + Kn_p \left(C_1 + C_2 e^{-C_3/Kn_p} \right) \quad (2.4)$$

Following this aerosol theory, Coimbra et al. (2021) derived a proper functional form of the slip function for smaller gas molecules as ratio of the molecular Reynolds number Re_{m_i} and the no-slip Reynolds number $Re_{j,ns}$ of the background gas, such that $C(Re_{m_i}) = Re_{m_i}/Re_{j,ns}$.

The molecular Reynolds number is calculated below.

$$Re_{m_i} = \frac{\bar{u}_i d_{k_i}}{2\nu_j} \quad (2.5)$$

where the mean velocity $\bar{u}_i = \sqrt{8RT/\pi M_i}$, d_{k_i} is the kinetic diameter of the diffusing molecule, and $Re_{j,ns}$ is a reference Reynolds number dependant on thermodynamic properties of the background gas and constant at any given values of temperature and pressure. The reference Reynolds number $Re_{j,ns}$ can be approximated as follows.

$$Re_{j,ns} \approx 3.39 \times 10^{-21} \frac{T^{\frac{5}{2}}}{P\nu_j^3} \quad (2.6)$$

In the work by Coimbra et al. (2021), they propose a functional form of the slip correction factor for diffusion in dry air such that $C(\cdot) = Re_{m_i}/Re_{j,ns}$. For diffusion in dry air under normal conditions $T = 298$ [K] and $P = 1$ atm, the slip correction factor is directly proportional to the molecular Reynolds number as $C(Re_{m_i}) = 7.35 \times 10^4 Re_{m_i}$. Using this constant of proportionality, a simple expression is proposed that can be used to accurately estimate Schmidt numbers for simple gases diffusing in air at normal conditions.

$$Sc_i = 0.11 \chi_i \sqrt{M_i} \quad (2.7)$$

where χ_i is the dynamic shape factor and M_i is the molecular mass of the diffusing gas.

In order to determine the shape correction factor χ_i , Dahneke (1973) specified a technique that can be used to approximate the slip correction factor for non-spherical bodies over the entire range of Kn_p based on a statistical average of all possible Brownian motion collision orientations. This is then adapted to find that particles with aspect ratios of 2 and 3 in free-molecule flow for diatomic, and triatomic molecules respectively, such that the work done by ratio of the adjusted length scale for simple non-spherical particles is valid over the entire range of Kn_p ,

from continuum (Stokes) to free molecule flows. The shape factors for these simple gases are then determined to be 1.23 and 1.39 for diatomic and triatomic molecules respectively Scheuch and Heyder (1990). However, at higher aspect ratios >3 the statistical average of all Brownian motion orientations proves insufficient and overestimates the dynamic shape factor and subsequently the binary diffusion coefficients of these molecules, such as organic compounds.

This work will seek to build on the adaptation of aerosol theory to the molecular level for simple gases by Coimbra et al. (2021) and extending it to more complex organic molecules diffusing in dry air at normal conditions, in particular, primary alcohols and linear hydrocarbons, such as n-paraffins, alkenes, alkynes.

Chapter 3

Methods

Many different definitions of a dynamic shape factor exist in literature, however for the purposes of this work the definition by Fuchs et al. (1964) will be used. This is given by

$$\kappa = \frac{F(v)}{F_{ve}(v)} = \frac{D_{ve}}{D} \quad (3.1)$$

where the subscript "ve" denotes a volume equivalent sphere for which $F(v)$ and D are the fluid drag force and the diffusion coefficient acting on an irregularly shaped non-spherical aerosol particle moving through a viscous fluid with velocity, v respectively. Therefore, the dynamic shape factor is defined based on the ratio of the drag force experienced by a non-spherical particle to the drag force experienced by a volume equivalent sphere traveling at the same velocity and medium (Scheuch and Heyder, 1990).

3.1 Bonding Configurations

In order to derive a functional form of the dynamic shape factor for organic molecules, the molecular shape of organic compounds is reviewed. For organic molecules, the focus of configuration is a carbon atom and the bonds originating from it. Bond configurations are predicted by Valence-Shell Electron-Pair Repulsion (VSEPR) theory developed by Gillespie and Hargittai (2013). This theory states that the geometry of a molecule is dependent on the repulsion of valence electron pairs and thus will adopt an arrangement in order to minimize this

repulsion. Therefore the overall shape of an organic molecule can be predicted based on the number of central carbon atoms which make up the backbone of these molecules.

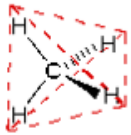
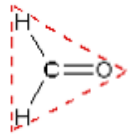

Configuration	Bonding Partners	Bond Angles	Example
Tetrahedral	4	109.5°	
Trigonal	3	120°	
Linear	2	180°	

Figure 3.1. Bonding configurations of carbon as predicted by the Valence-Shell Electron-Pair Repulsion (VSEPR) theory, including bonding partners and corresponding angles (Reusch, 2013).

For organic carbon based molecules, there are only three categories of bonding configurations; linear, trigonal planar, and tetrahedral hybridization as shown in Figure (3.1). These bonding configurations depend on the type of covalent bond between the carbon atoms, such that single, double, and triple bond(s) correspond to tetrahedral, trigonal planar, and linear hybridization respectively. Therefore any dynamic shape factor form must be classified according to the number of covalent bonds between the carbon atoms. As such, the dynamic shape factor developed in this work is separated by class of organic molecules, such that a correlation exists for normal alkanes (single bond), alkenes (double bond), and alkynes (triple bond). Primary alcohols are also included in this work as they have a tetrahedral bonding configuration similar to that of n-alkanes but are considered to have a different shape factor correlation due to the presence of an oxygen atom and subsequent hydroxide (OH) group.

Other organic compounds that exist and are excluded in this work are due to the non-linearity of their molecular geometry due to bent or cyclical structures and the limitations of

existing experimental data for the diffusion of these compounds in air at normal conditions.

3.2 Quantitative Analysis

In agreement with the VSEPR theory and bonding configurations, a function form of the dynamic shape factor must then be related to the number of carbon atoms n that make up the backbone of these linear molecules.

$$\chi_i = f(n) \quad (3.2)$$

An extensive literature review was conducted whereby published experimental and numerical binary diffusion coefficients for organic compounds diffusing in air at normal conditions $T=298$ [K] and $P=1$ atm. In particular, the compilation of gas phase diffusion coefficients by Tang et al. (2015) was extensively used for experimental data. Where this experimental data was incomplete, numerical values were obtained from the property data tabulations as a function of temperature listed in Yaws (2014) and noted respectively. These were compiled and a qualitative analysis was conducted using Python, in order to determine a functional form of a dynamic shape factor based on fitting this data using the correlation developed by Coimbra et al. (2021) shown in Equation (2.7) above.

In comparing the results to the CE theory mentioned previously, the Python "thermo" package (Bell, 2017) was used extensively particularly in regards to computing the collision diameters listed above using the correlations in Equations (1.2-9). For the Fuller method, Equation (1.11) was used in conjunction with the values for diffusion volume increments listed above. Collision diameters were used in place of kinetic and molecular diameters to determine the Stokes friction factor, and binary diffusion coefficients developed using the Chapman-Enskog theory to determine the slip correction factors for both simple gases and organic compounds diffusing in dry air under normal conditions.

Chapter 4

Results

4.1 Dynamic Shape Factor

The dynamic shape factor χ_i for higher atom species, such as those in organic compounds, can be calculated by a simple power law rule that depends only on the number of carbon atoms of the molecule n and two coefficients that are unique to the class of organic molecules. These coefficients are found by curve-fitting the expression to the experimental and numerical data.

$$\chi_i = c_0 \cdot n^{c_2} \quad (4.1)$$

where n is the number of carbon atoms and c_0 and c_2 are coefficients for the respective organic compound species listed below.

Table 4.1. Coefficients for Determining Dynamic Shape Factors χ_i for Calculating Binary Diffusion Coefficients in Organic Compounds Diffusing in Air at Normal Conditions

Gas i	Symbol	c_0	c_2
n-alkanes	C_nH_{2n+2}	1.64	0.102
alkenes	C_nH_{2n}	1.32	0.205
alkynes	C_nH_{2n-2}	1.65	0.059
alcohols	$C_nH_{2n+2}O$	1.34	0.289

This simple power law expression can be used to compute the dynamic shape factors of organic compounds and combined with the Schmidt number correlation in Equation (2.7) to provide a quick and highly accurate estimation of Sc_i values for organic compounds that only depends on the molecular weight of the compound and the number of carbon atoms contained therein, both of which are mutually related. This simplification removes need for complex force potentials that require gas properties and volume increments required for CE theory and Fuller method respectively.

4.2 Binary Diffusion Coefficients

Using the correlation proposed above, Schmidt numbers and binary diffusion coefficients can then simply be calculated for organic molecules diffusing in air in normal conditions by adapting Equation (2.7) as follows.

$$Sc_i = c_1 \cdot n^{c_2} \sqrt{M_i} \quad (4.2)$$

$$D_{ij} = \frac{v_j}{c_1 \cdot n^{c_2} \sqrt{M_i}} \quad (4.3)$$

where c_1 is introduced and given in the table below.

Table 4.2. Coefficients for determining binary diffusion coefficients Sc_i and D_{ij} for organic compounds diffusing in dry air at normal conditions T=298 [K] and P=1 atm

Gas i	Symbol	c_1	c_2
n-alkanes	C_nH_{2n+2}	0.18	0.102
alkenes	C_nH_{2n}	0.15	0.205
alkynes	C_nH_{2n-2}	0.18	0.059
alcohols	$C_nH_{2n+2}O$	0.15	0.289

Chapter 4, is currently being prepared for submission for publication of the material. Dynamic Shape Factors for Binary Diffusion of Organic Compounds in Air 2021. Lubega, Nathan H; Nguyen, Anthony; Coimbra, Carlos F.M. The thesis author was the primary investigator and author of this material.

Chapter 5

Discussion

The results indicate that the functional form of the dynamic shape factor can be represented by a simple power law function based on a geometrical analysis of the molecular shape of organic molecules. By applying the Valence-Shell Electron-Pair Repulsion theory to understand the bonding configurations of these molecules based on the number of carbon atoms and number of covalent bonds, dynamic shape factors can be determined for a whole class of organic compounds diffusing in air under normal conditions $T=298$ [K] and $P=1$ atm.

5.1 Slip Correction for Organic Molecules

Subsequently, binary diffusion coefficients and Schmidt numbers can then be determined with the computed dynamic shape factors and the aerosol theory of particle diffusion based on Brownian motion of a spherical particle can be utilized for non-spherical organic compounds. This is possible based on the relationship developed by Coimbra et al. (2021) for the slip correction factor for simple gases. Therefore, for completeness, it is shown that the technique developed by Coimbra et al. (2021) for simple gases applies to longer and more complex molecules contained in organic compounds. Thus, the slip correction factor $C(\cdot)$ is plotted for various organic compounds and compared to that of simple gases to show that it is directly proportional to the molecular Reynolds number by $C(Re_{m_i}) = 7.35 \times 10^4 Re_{m_i}$ with a high

coefficient of determination $R^2 > 0.99$. This is shown in Figure (5.1) below.

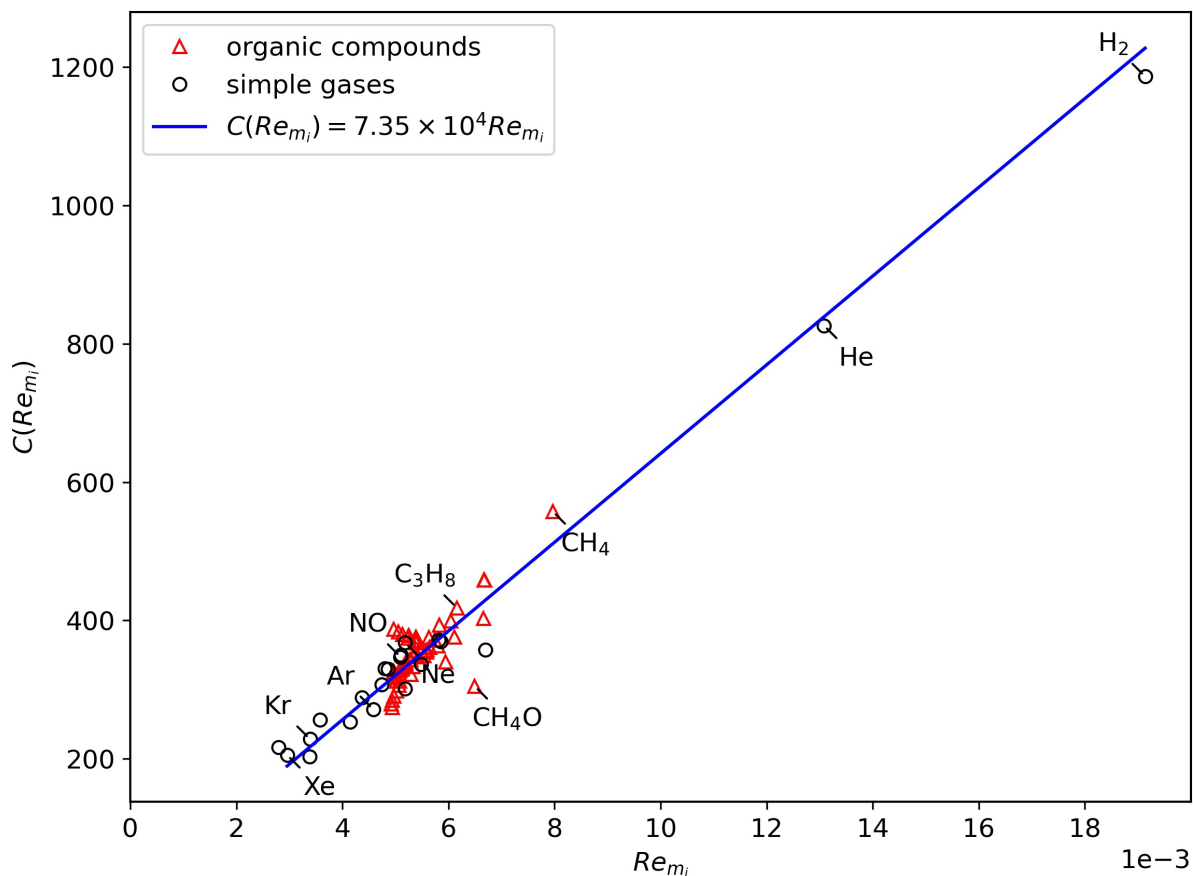


Figure 5.1. The slip correction factor $C(\cdot)$ as a function of the molecular Reynolds number Re_{m_i} . The circle values correspond to the values of $C(\cdot)$ in Equations (1) and (2) that return the exact values given by the CE theory in Table I. The high coefficient of determination ($R^2 > 0.99$) in this figure corroborates the choice of the functional form for $C(\cdot) = Re_{m_i}/Re_{j,ns}$, as well as the use of kinetic diameters d_{k_i} as the proper molecular length scale in Re_{m_i}

5.2 Model Validity

To determine the validity of the proposed model, Schmidt numbers developed by the correlation proposed in Equation (4.2) were compared to those collected using the Chapman-Enskog theory and Fuller method(s) for similar organic compounds under the same conditions of temperature and pressure. These results were also compared to existing experimental data, where available, and plotted against the molecular weight as shown in Figure (5.2). The results

have been tabulated for the first 8 carbon atoms in each class of organic molecules reviewed and the mean deviation included beside each molecule for all the methods used in this analysis.

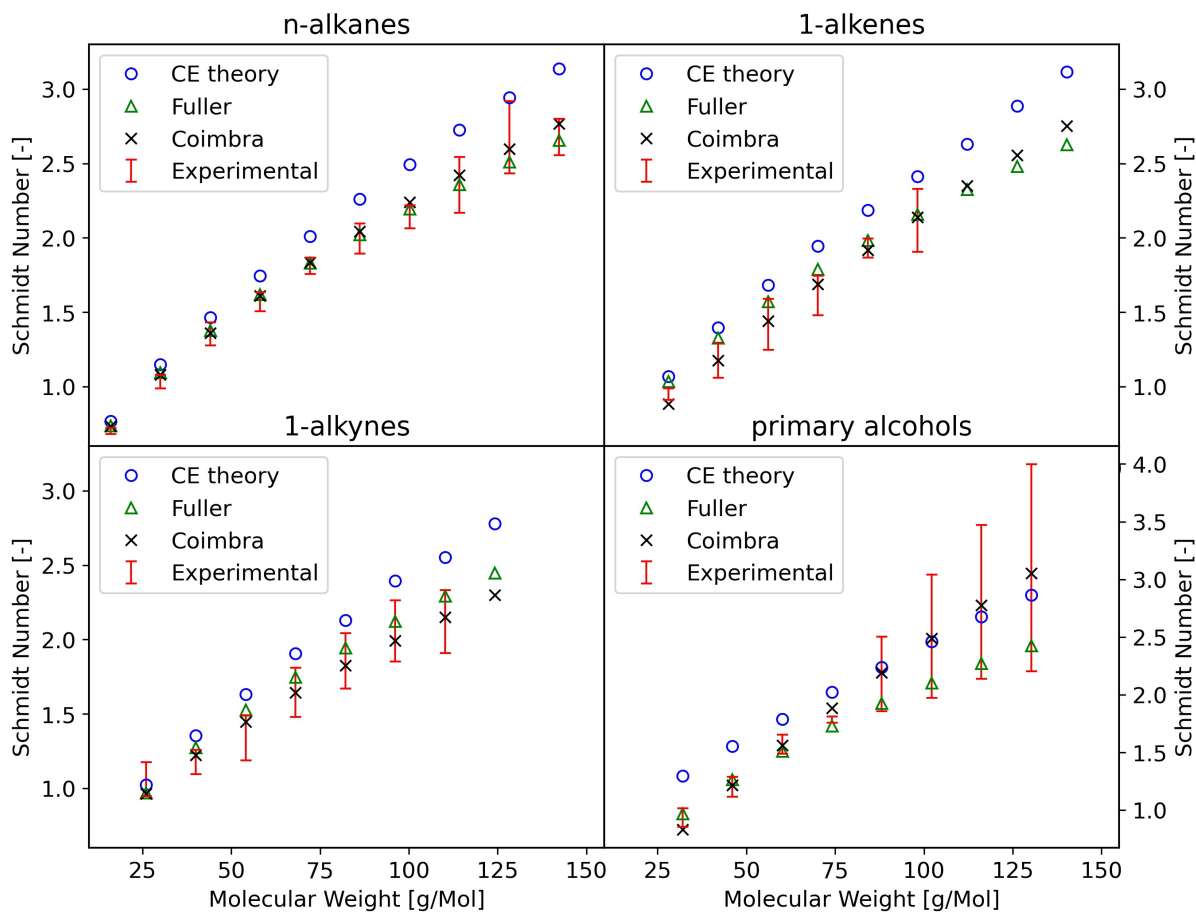


Figure 5.2. Schmidt numbers as a function of molecular weight for different groups of organic compounds diffusing in dry air under normal conditions $T = 298$ [K] and $P = 1$ atm. Circles show values calculated with the Chapman-Enskog (CE) theory with the 6-12 Lennard-Jones potential, triangles are determined with the semi-empirical Fuller (F) method, crosses denote those determined using the power law expression presented combined with the Coimbra (C) aerosol theory, and vertical bars correspond to the range of values reported in experimental results

The following observations can be made. First, as expected the Fuller (F) method overestimates binary diffusion coefficients and subsequently understates Schmidt numbers which are an inverse of the diffusion coefficient. This is likely due to the fact the sum of the atomic diffusion volumes does not add up to the total molecular volume and this effect is more

pronounced in longer atoms as diffusion volume increments were empirically determined for simple and lower molecular weight compounds diffusing in air.

Second, the Chapman-Enskog (CE) theory likely over predicts the Schmidt numbers and this effect is more pronounced as the molecular weight increases. It is likely that is a function of the empirical correlation used to determine the collision diameters given in Equations (1.2) and (1.3) by Bird et al. (2006). It is highly probable that these results would differ for other correlations and no determination can be made with certainty in this regard. However, such uncertainties are not uncommon in CE theory as empirical correlations are all developed based on fitting data for a select few molecules.

Third, the range of uncertainty of the experimental results is a major point of note for determining binary diffusion coefficients. In particular, as seen with primary alcohols, the uncertainty increases significantly as the molecular weight increases, that is, heavier molecules, are much more difficult to measure. This makes the challenge of determining experimental coefficients even more difficult. Therefore, a way to extrapolate binary diffusion coefficients over a larger range of species is necessary.

The semi-empirical correlation proposed in Equation (4.2) provides a geometric alternative that can be used to provide accurate diffusion coefficients based on the number of carbon atoms and the molecular weight of the molecule within a mean $\pm 4\%$ deviation compared to experimental results. This deviation lies within the acceptable margin of uncertainty of existing and widely accepted methods such as Chapman-Enskog theory and Fuller method which have a $\pm 6\%$ and $\pm 7\%$ bias respectively. The values of the dynamic shape factor and Schmidt numbers used in this analysis have been compiled and the mean deviation computed for each molecule.

Table 5.1. Shape factors χ_i calculated from the proposed correlation and computed Sc_i comparison with the Chapman-Enskog (CE) theory, Coimbra’s model (C), and Fuller’s model (F) for the molecules listed in Table I. Comparing the C and F models and most widely accepted values obtained by the CE theory against the experimental results (EXP), we find that the mean bias deviation is . The values of Δ_{CE} , Δ_C and Δ_F are the relative deviations with respect to $Sc_{i,EXP}$.

Gas i	Symbol	n	χ_i	$Sc_{i,E}$ range	$Sc_{i,CE}$	$\Delta_{CE}(\%)$	$Sc_{i,C}$	$\Delta_C(\%)$	$Sc_{i,F}$	$\Delta_F(\%)$
methane	CH ₄	1	1.64	0.680 – 0.722 ^a	0.767	+9	0.734	+5	0.739	+5
ethane	C ₂ H ₆	2	1.76	0.988 – 1.078 ^a	1.148	+11	1.079	+4	1.097	+6
propane	C ₃ H ₈	3	1.84	1.276 – 1.432 ^a	1.464	+11	1.362	+1	1.379	+2
butane	C ₄ H ₁₀	4	1.89	1.508 – 1.633 ^a	1.745	+13	1.610	+3	1.619	+3
pentane	C ₅ H ₁₂	5	1.94	1.756 – 1.868 ^a	2.011	+17	1.835	+1	1.830	+1
hexane	C ₆ H ₁₄	6	1.97	1.895 – 2.098 ^a	2.259	+16	2.043	+2	2.021	+1
heptane	C ₇ H ₁₆	7	2.00	2.064 – 2.213 ^a	2.494	+10	2.238	+5	2.196	+3
octane	C ₈ H ₁₈	8	2.03	2.167 – 2.544 ^a	2.724	+17	2.422	-3	2.359	0
ethene	C ₂ H ₄	2	1.55	0.912 – 0.988 ^a	1.069	+13	0.884	-7	1.035	+9
propene	C ₃ H ₆	3	1.66	1.060 – 1.296 ^a	1.397	+18	1.177	0	1.328	+12
1-butene	C ₄ H ₈	4	1.75	1.248 – 1.590 ^a	1.683	+19	1.442	+2	1.574	+11
1-pentene	C ₅ H ₁₀	5	1.82	1.481 – 1.746 ^a	1.946	+21	1.688	+5	1.789	+11
1-hexene	C ₆ H ₁₂	6	1.88	1.868 – 1.994 ^a	2.187	+13	1.919	-1	1.983	+3
1-heptene	C ₇ H ₁₄	7	1.93	1.905 – 2.329 ^b	2.414	+14	2.140	+1	2.161	+2
1-octene	C ₈ H ₁₆	8	2.01	2.306 – 2.502 ^a	2.629	+9	2.351	-2	2.326	-3
ethyne	C ₂ H ₂	2	1.72	0.946 – 1.176 ^a	1.024	-3	0.963	-9	0.972	-8
propyne	C ₃ H ₄	3	1.76	1.095 – 1.260 ^a	1.354	+15	1.224	+4	1.275	+8
1-butyne	C ₄ H ₆	4	1.79	1.186 – 1.490 ^a	1.631	+21	1.446	+8	1.527	+14
1-pentyne	C ₅ H ₈	5	1.81	1.481 – 1.810 ^b	1.906	+16	1.645	0	0.972	+6
1-hexyne	C ₆ H ₁₀	6	1.83	1.670 – 2.042 ^b	2.130	+15	1.826	-2	1.275	+5
1-heptyne	C ₇ H ₁₂	7	1.85	1.852 – 2.264 ^b	2.394	+16	1.993	-3	1.527	+3
1-octyne	C ₈ H ₁₄	8	1.86	1.908 – 2.332 ^b	2.552	+20	2.151	+1	1.527	+8
methanol	CH ₄ O	1	1.33	0.853 – 1.016 ^a	1.293	+38	0.830	-11	0.968	+3
ethanol	C ₂ H ₆ O	2	1.63	1.116 – 1.288 ^a	1.553	+29	1.216	+1	1.263	+5
1-propanol	C ₃ H ₈ O	3	1.83	1.487 – 1.655 ^a	1.786	+14	1.562	-1	1.511	-4
1-butanol	C ₄ H ₁₀ O	4	1.99	1.758 – 1.812 ^a	2.021	+13	1.885	+6	1.729	-3
1-pentanol	C ₅ H ₁₂ O	5	2.12	1.858 – 2.504 ^a	2.235	+2	2.193	+1	1.925	-12
1-hexanol	C ₆ H ₁₄ O	6	2.24	1.973 – 3.039 ^a	2.460	-2	2.488	-1	2.104	-16
1-heptanol	C ₇ H ₁₆ O	7	2.34	2.137 – 3.472 ^a	2.674	-5	2.774	-1	2.271	-19
1-octanol	C ₈ H ₁₈ O	8	2.43	2.202 – 3.997 ^a	2.862	-8	3.053	-2	2.427	-22

Chapter 6

Conclusion

This work advances our understanding and modeling of gaseous diffusion in air that is a key physical processes in our atmosphere on earth. By applying spherical aerosol theory to the molecular level using the slip correction factor developed for simple gases, a geometric model is developed to determine the dynamic shape factors of non-spherical molecules, specifically linear organic compounds. The semi-empirical correlation proposed provides a simple and robust alternative that can be used to provide accurate diffusion coefficients for organic compounds diffusing in dry air under normal conditions $T=298$ [K] and $P=1$ atm. This functional form of the dynamic shape factor is based on the number of carbon atoms that makeup the backbone of the molecule and the number of covalent bonds originating from them. Separate classes of organic molecules were divided by their covalent bonds and through the application of VSEPR theory, associated bonding configurations were deduced that can predict the shape of the molecule. These were divided into normal alkanes, alkynes, and alkenes for single, double, and triple bond respectively. Primary alcohols were also included as they also contain a single covalent bond.

A simple power law expression was developed of the form $\chi_i = c_0 \cdot n^{c_2}$ to calculate the dynamic shape factor of these organic molecules. The coefficients c_0 , c_1 , and c_2 have been included in Tables (4.1) and (4.2) and are determined empirically from fitting experimental and numerical data to the functional form of the slip correction factor developed by Coimbra et al. (2021). By using the molecular weight of the molecule, such that $Sc_i = c_1 \cdot n^{c_2} \sqrt{M_i}$ the Schmidt

number can be determined with a mean $\pm 4\%$ deviation compared to experimental results and within the uncertainty range $\pm 6\%$ and $\pm 7\%$ of the CE theory and Fuller method respectively.

This correlation is useful to determine binary diffusion coefficients of higher atom species diffusing in our atmosphere that may be otherwise impossible to determine due to difficulty in conducting diffusion experiments and can be extrapolated to species lacking physical property data provided they fall in the class of molecule evaluated. Furthermore, more linear organic molecules, such as esters, can be added to this functional form and coefficients can be determined from experimental data as necessary. However, the dynamic shape factor for non-linear organic molecules, such as branched or cyclic hydrocarbons, or aromatic compounds, cannot be determined with this geometrical technique as the carbon atoms alone are not a suitable proxy to determine the shape of the molecule.

The method presented in the work can be used to reduce the complexities involved in modeling diffusion coefficients, particular in larger climate simulations while still maintaining a reasonable degree of accuracy and robustness within normal atmospheric conditions.

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