

THE MEAN FREE PATH IN AIR

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Abstract—Values for the mean free path l in air are presented for temperatures 15, 20, 23 and 25°C for both dry air and moist air at relative humidities of 50 and 100%, at atmospheric pressure (1.01325×10^5 Pa) and at pressure 1×10^5 Pa. Use is made of an expression which minimizes the dependence on physical 'constants' for mean free path:

$$l = \sqrt{\frac{\pi}{8}} \cdot \frac{\mu}{u} \cdot \frac{1}{\sqrt{\rho P}},$$

where μ is the viscosity of air, ρ is the density of air, P is the pressure and u is a numerical factor equal to 0.4987445. Differences of up to 1.6% were obtained between the values of mean free path at 23°C from this work and that of other workers. Comparison between the Cunningham slip correction factor from the present work and that from other work shows differences up to 1.8%.

NOMENCLATURE

- A, B, c Coefficients in the Knudsen–Weber slip correction equation for Stokes' drag force
- C Slip correction factor
- \bar{C} Mean molecular speed (ms^{-1})
- Kn Knudsen number defined as l/r
- M_a Molecular weight of air (= 28.962458)
- M_v Molecular weight of water (= 18.0152)
- N_A Avogadro's constant (= 6.0221358×10^{26} kmole $^{-1}$)
- P Pressure (Pa)
- P_0 Some 'standard' pressure
- R Universal gas constant (= 8.31448×10^3 JK $^{-1}$ kmole $^{-1}$)
- T Temperature (K)
- T_0 Some 'standard' temperature
- $Z(P, T)$ Compressibility factor
- e_s Saturation vapour pressure of water vapour over a plane surface of pure liquid water
- $f(P, T)$ Enhancement factor
- k Boltzmann's constant (= 1.380653×10^{-23} JK $^{-1}$)
- l Mean free path in air (m)
- l_0 Mean free path in air at a 'standard' temperature and pressure
- r Particle radius (micrometers, μm)
- u Numerical factor (= 0.4987445 in this work)
- x_i Mole fraction for gas constituent i
- ρ Density of air (kg m^{-3})
- μ Viscosity of air ($\text{kg m}^{-1} \text{s}^{-1}$)

INTRODUCTION

In aerosol physics, there is often a need to know the terminal fall velocity, mobility, or diffusion coefficient (diffusivity) of particles. In the Stokes' regime, all of the above properties are described by equations which incorporate the so-called Cunningham (1910) slip correction C which is dependent on the mean free path of air. The slip correction C multiplies the Stokes' fall velocity, the mobility and diffusion coefficient to yield the correct values. Thus, accurate determination of the fall velocity, mobility and diffusion coefficient of particles is dependent on accurate knowledge of the mean free path l in air.

As pointed out by Fuchs (1964), the transfer rates of momentum, energy and mass are determined by the value of the Knudsen number $Kn = l/r$, where r is the particle radius. In the limiting cases of very small and very large Knudsen numbers, the theories of these transfer processes are exact. Thus, for example, in the case of small Knudsen numbers, $l/r \rightarrow 0$, diffusional growth or evaporation for particles (or droplets) is described by classical

continuum diffusion and heat transfer theories, assumed valid to within about one mean free path distance from the particle. When the mean free path is large compared to the size of an evaporating (or growing) particle, classical kinetic theory can be applied in this so-called free-molecule regime (Hidy and Brock, 1970) to determine the evaporation or growth rate. Progress in the theory of particle transport processes at intermediate Kn values has been reviewed by Fuchs and Sutugin (1970). They point out that the theory of transport to aerosol particulates constantly makes use of the concept of the mean free path of gas molecules.

Despite the importance of accurately knowing the mean free path l in air, few reliable values of l have been published and indeed different mean free path values have appeared in the literature for the same temperature. In this paper the expression for the mean free path is presented first. In the next section, expressions for the density of dry and moist air, required in the evaluation of mean free path, are given together with physical constants used to evaluate the air density. This is followed by a section on the viscosity of dry and moist air. Tabulated values of the viscosity of air and the mean free path in air are presented for temperatures of 15, 20, 23 and 25°C for relative humidities of 0, 50 and 100% at pressures 10^5 and 1.01325×10^5 Pa. Finally comparison is made between the newly computed value of mean free path at 23°C, 1.013×10^5 Pa, with that of other workers. In addition, Cunningham slip correction values on the mean free path from this work and from currently used mean free path values are inter-compared.

THEORY

The mean free path, l , in air is given by the expression (Chapman and Cowling, 1970):

$$l = \frac{\mu}{u} \cdot \frac{1}{\rho \bar{C}}, \quad (1)$$

where ρ is the density of the air molecules, \bar{C} is the mean molecular speed, and μ is the coefficient of viscosity of air.

The numerical factor u , equal to 0.4987445 is fractionally smaller than the normally quoted value of 0.499 (Chapman and Cowling, 1970) due to the recalculation of the coefficient of viscosity by Pekeris and Altermann (1957), who, like Chapman and Cowling (1970), modelled the gas molecules as rigid elastic spheres.

Equation (1) reduces to

$$l = \sqrt{\frac{\pi}{8}} \frac{\mu}{u} \frac{1}{\sqrt{\rho P}}, \quad (2)$$

where P is the atmospheric pressure. Since $\rho \sim 1/T^{1/2}$ under the assumption that the gas molecules obey the equation of state we have

$$l/l_0 = (\mu/\mu_0) \cdot (P_0/P) \cdot (T/T_0)^{1/2}, \quad (3)$$

where the subscript '0' denotes the value at some 'standard' temperature and pressure. Equation (3) is strictly applicable for dry air. The mean free path l at some pressure and temperature at which the viscosity μ is known can be determined from the known value of mean free path l_0 at a 'standard' pressure P_0 and temperature T_0 through use of equation (3). Since the density ρ is contained in the expression for mean free path [equation (2)], formulae for the density of dry and moist air are presented in the following section.

DENSITY OF DRY AND MOIST AIR

The density of dry air, ρ , is given by:

$$\rho = \frac{PM_a}{RTZ}, \quad (4)$$

where P is the pressure, M_a is the molecular weight of air, R is the universal gas constant and

Z is the compressibility factor of the non-ideal gas (air) which is a function of pressure P and temperature T . Tabulated values of Z for a range of P and T values for dry and moist air are given in the *Smithsonian Meteorological Tables* (1966), based on the data provided by Goff and Gratch (1945).

The density of moist air is obtained from the expression

$$\rho_{\text{moist air}} = \frac{PM_a}{RTZ} \left[1 - \left(1 - \frac{M_v}{M_a} \right) \frac{R.H. f e_s}{100 P} \right], \quad (5)$$

where M_v is the molecular weight of water, $R.H.$ is the relative humidity, and e_s is the saturation vapour pressure of the pure vapour (without the admixture of air) over a plane surface of pure liquid water. A complicated expression for the enhancement factor f involving a series of virial coefficients was derived by Hyland and Wexler (1973) and is used by Hyland (1975) to obtain enhancement values for air over water from -80°C to 90°C at 10°C intervals and for a wide range of pressures including 10^5 Pa (1 bar).

VALUES OF THE PARAMETERS USED IN THE EXPRESSION FOR DENSITY OF DRY AND MOIST AIR

A new preliminary adjusted value from a new least-squares adjustment currently made to the universal gas constant R (Dr B. N. Taylor, NBS, Gaithersburg, private communication, 1986) is taken to be

$$R = 8.31448 \times 10^3 \text{ JK}^{-1} \text{ kmole}^{-1}.$$

The molecular weight of air, M_a , calculated from:

$$M_a = \sum_{i=1}^n x_i M_i,$$

where M_i is the molecular weight of an individual constituent and x_i is the corresponding mole fraction, is taken to be:

$$M_a = 28.962458,$$

using the constituent values given by Jones (1978). This assumes a mole fraction of 0.00033 for CO_2 in the atmosphere, in close agreement with currently quoted values (Komhyr *et al.*, 1985). Values of the compressibility factor Z were linearly extrapolated from the *Smithsonian Meteorological Tables* (1966).

The molecular weight of water, M_v , was taken to be 18.0152 (International Union of Pure and Applied Chemistry, 1976). The saturation vapour pressure e_s of pure water vapour was taken from Wexler (1976).

The enhancement factor f was taken to be 1.004 over the temperature range used here (15 – 25°C) at pressures 10^5 Pa and 1.01325×10^5 Pa from an examination of the tabulated values of Hyland (1975).

The constants used in the density calculations are listed in Table 1. Values of density of dry air using equation (4) and of moist air using equation (5) for relative humidities of 50 and 100% are presented in Table 2 for pressures of 10^5 Pa and 1.01325×10^5 Pa.

VISCOSITY OF AIR

As indicated by equation (2), the mean free path is linearly dependent on the viscosity of air. A survey of the literature revealed that among the wide variability of viscosity values, the best available data for the viscosity (dynamic) of air at 1 atm (1.01325×10^5 Pa) is as shown in Table 3.

The values outlined in Table 4 are those adopted for use in this work. The effect of changing pressure from 1×10^5 Pa to 1.013×10^5 Pa at constant temperature upon the viscosity of air is negligible.

Table 1. Physical constants used in the calculation of density

Parameter	Symbol	Value	Uncertainty	Reference
Universal gas constant	R	8.31448×10^3 $\text{JK}^{-1} \text{kmole}^{-1}$	25 ppm	NBS—private communication by Dr B. N. Taylor
Molecular weight of air	M_a	28.962458	$\pm 4 \times 10^{-5}$	Jones (1978)
Compressibility factor	Z	Function of temperature and pressure	$\pm 1.7 \times 10^{-5}$	Smithsonian Meteorological Tables (1966)
Molecular weight of water	M_v	18.0152	± 0.0005	International Union of Pure and Applied Chemistry (1976)
Saturation water vapour pressure	e_s		Does not exceed 64 ppm over temperature range 15–25°C	Wexler (1976)
Enhancement factor	f	1.004	± 0.00013	Hyland (1975)

Table 2. Density of dry and humid air

Temperature (K)	Pressure (Pa)	Relative humidity (%)		
		0	50	100
288.15	10^5	1.2094	1.2055	1.2017
	1.0325×10^5	1.2254	1.2215	1.2177
293.15	10^5	1.1887	1.1834	1.1783
	1.01325×10^5	1.2045	1.1992	1.1940
296.15	10^5	1.1766	1.1704	1.1642
	1.01325×10^5	1.1922	1.1860	1.1798
298.15	10^5	1.1687	1.1617	1.1548
	1.01325×10^5	1.1842	1.1772	1.1703

Table 3. Viscosity of air

(a) Viscosity of dry air

Temperature (°C)	Measured value ($\text{kg m}^{-1} \text{s}^{-1}$)	Uncertainty	Author(s)	Reference
20	1.8192×10^{-5}	0.00006	Bearden (1939)	<i>Phys. Rev.</i> 56 , 1023
20	1.8194×10^{-5}	0.00035	Kestin and Leidenfrost (1959)	<i>Physica</i> 25 , 1033
25	1.8446×10^{-5}	0.00091	Kestin and Leidenfrost, (1959)	<i>Physica</i> 25 , 1033

(b) Viscosity of moist air

Temperature (°C)	Relative humidity (%)		Uncertainty	Author(s)	Reference
	50	100			
20	1.815×10^{-5}	1.8127×10^{-5}	0.1%	Hochrainer and Munczak (1966)	<i>Sber. öst. Akad. Wiss., Math. Klasse Abt. II</i> , 175 , 539
25	1.8420×10^{-5}	1.8400×10^{-5}	$\pm 0.1\%$	Kestin and Whitelaw (1964)	<i>Int. J. Heat Mass Transfer</i> 7 , 1245

Calculated values of mean free path

Values for the mean free path in air using viscosity values of Table 4 and density values derived from equations (4) and (5) are given in Table 5. The values are rounded off to the fourth significant figure. The mean free path is inversely proportional to air pressure for dry air as readily verifiable from Table 5. Mean free path values are also given at a second pressure of 10^5 Pa since the mean free path is not quite inversely proportional to pressure for moist air at the fourth significant figure. (Inverse proportionality does, however, obtain at the third significant figure.)

DISCUSSION

While it is realized that one has as many free paths as there are kinds of binary collisions between the air constituent molecules, the simplest approach is to treat air as a single component gas possessing an average density, viscosity and mean free path at a particular temperature and pressure.

Recent use of the Chapman-Enskog theory as applied to multi-component gases of a gas mixture, by Hirschfelder *et al.* (1964) together with the use of the law of corresponding states as formulated by Kestin *et al.* (1972) has permitted the calculation of transport properties (including viscosity) of multi-component dilute mixtures of gases at densities where binary collisions between the components are dominant. These theories have been successfully applied (Hellemans *et al.*, 1973) to the calculation of the viscosity of air, treated as a ternary

Table 4. The air viscosity values adopted for use in this work

(a) Viscosity of dry air

Temperature (°C)	Viscosity of air at 1.013×10^5 Pa ($\text{kg m}^{-1} \text{s}^{-1}$)	Comments
20	1.8192×10^{-5}	Bearden's (1939) value, listed in the <i>American Institute of Physics Handbook</i> (1972)
25	1.8446×10^{-5}	Kestin and Leidenfrost (1959) value
23	1.8353×10^{-5}	Based on Bearden's (1939) value at 20°C and using temperature increment of $0.00536 (\text{kg m}^{-1} \text{s}^{-1})/^\circ\text{C}$ calculated from Kestin and Leidenfrost (1959) measurements at 20 and 25°C.
15	1.7924×10^{-5}	Using temperature 'decrement' of $0.00536 (\text{kg m}^{-1} \text{s}^{-1})/^\circ\text{C}$, together with Bearden's value at 20°C.

(b) Viscosity of moist air

Temperature (°C)	Viscosity of moist air at 1.013×10^5 Pa ($\text{kg m}^{-1} \text{s}^{-1}$)		Comments
	Relative humidity (%)		
	50	100	
20	1.8154×10^{-5}	1.8127×10^{-5}	Hochrainer and Munczak (1966) values
25	1.8420×10^{-5}	1.8400×10^{-5}	Kestin and Whitelaw's (1964) values
23	1.8314×10^{-5}	1.8291×10^{-5}	Interpolation of viscosity values at 20 and 25°C
15	1.7888×10^{-5}	1.7854×10^{-5}	Extrapolation based on viscosity measurements at 20 and 25°C

Table 5. Mean free path in air

Temperature (K)	Pressure (Pa)	Relative humidity (%)		
		0*	50 (10^{-8} m)	100
288.15	1.01325×10^5 10^5	6.391	6.389	6.386
		6.476	6.473	6.471
293.15	1.01325×10^5 10^5	6.543	6.544	6.548
		6.630	6.631	6.635
296.15	1.01325×10^5 10^5	6.635	6.638	6.647
		6.723	6.726	6.736
298.15	1.01325×10^5 10^5	6.691	6.701	6.714
		6.780	6.790	6.803

* Mean free path values for dry air can be determined at other temperatures and pressures through the use of equation (3).

mixture of nitrogen, oxygen and argon yielding excellent agreement between the calculated and experimental values for viscosity of air at 25°C (DiPippo and Kestin, 1968). This strengthens the justification for use of a mean free path based on a measured value for viscosity of air using equation (2). The mean free path calculation also relies on the use of an average value for the density of air. The procedure for obtaining air density using the molecular weights of individual air constituents based on their mole fractions gives good agreement with published values [*Smithsonian Meteorological Tables* (1966)].

The use of equation (2) for the mean free path $l = \sqrt{\pi/8} (\mu/u)(1/\sqrt{\rho P})$ has the merit of minimizing the use of physical constants as compared to using the more usual formulation for l

$$l = \frac{\mu}{u} \frac{1}{\rho \bar{C}}. \quad (6)$$

Equation (6) uses the value of $\bar{C} = (8kT/\pi m)^{1/2}$ which depends on k , M_a and N_A , 'constants' which undergo readjustment in value periodically. The value of the numerical factor u arises from the use of the molecular model of smooth rigid elastic spherical molecules. This is generally regarded as the more correct model for a rarified homogeneous molecular gas. Allen and Raabe (1982) base their mean free path determination ($l = 6.73 \times 10^{-8}$ m at 23°C) on the repulsive force molecular model which assumes that the gas molecules possess the same electric charge polarity. The repulsive force molecular theory yields a value for numerical factor of $5\pi/32$ (0.49087) in the expression for mean free path. The mean free path value derived in this work equals 6.635×10^{-8} m at temperature 23°C based on the more usually preferred rigid elastic spherical model, which employs the numerical factor of $1.016034 \times (5\pi/32)$ in the expression for the mean free path. The percentage difference of 1.4% between the two mean free path values is largely accounted for by the difference in the values of the numerical factors.

Davies (1945) uses a mean free path value of 6.609×10^{-8} m at 23°C through employment of the numerical factor of 0.499 ($5\pi/32 \times 1.016$). This mean free path value is within 0.4% of the value obtained in this work. Fuchs (1964), though using the same numerical factor as Davies (1945) above, quotes a value of 6.53×10^{-8} m. This is considered to be an underestimate and is more representative of the calculated mean free path at 20°C rather than at 23°C.

Hitherto, the mean free path in air has usually been calculated at a temperature of 23°C, to coincide with the temperature at which the majority of Millikan's (1923) work on the slip correction coefficients related to his electronic charge work, was carried out. This present work extends the mean free path calculations to a range of temperatures from 15 to 25°C. In addition, the work includes for the first time a presentation of mean free path values for moist air—at relative humidities of 50 and 100%. The results in Table 5 show that relative humidity

Table 6. Cunningham slip correction factor for dry air at 23°C, 1.013×10^5 Pa

Reference	Mean free path (10^{-8} m)	Cunningham slip correction formula	Knudsen number			
			0.01	0.1	1	10
Davies (1945)	6.609	$1 + Kn \left[1.257 + 0.400 \exp \left(-\frac{1.10}{Kn} \right) \right]$	1.0126	1.1257	2.390	17.153
Fuchs (1964)	6.53	$1 + Kn \left[1.246 + 0.418 \exp \left(-\frac{0.867}{Kn} \right) \right]$	1.0125	1.1246	2.422	17.293
Allen and Raabe (1982)	6.673	$1 + Kn \left[1.155 + 0.471 \exp \left(-\frac{0.596}{Kn} \right) \right]$	1.0116	1.1156	2.415	16.988
This work	6.635	$1 + Kn \left[1.252 + 0.399 \exp \left(-\frac{1.10}{Kn} \right) \right]$	1.0125	1.1252	2.387	17.087

has greatest influence on the mean free path ($\sim 0.3\%$ increase) at the higher temperatures. It can also be seen that relative humidity causes a small decrease ($\sim 0.1\%$) in the mean free path over the value for dry air at the lowest temperature (15°C) considered.

The mean free path directly affects the so-called Cunningham (1910) slip correction factor C , later modified by Knudsen and Weber (1911) to the form

$$C = 1 + Kn[A + B \exp(-c/Kn)]. \quad (7)$$

Since aerosol properties such as the Stokes' fall velocity, particle mobility and diffusivity are linearly dependent on the value of the slip correction C , accurate determination of these properties is dependent on accurate knowledge of the mean free path. Values of mean free path together with calculated Cunningham slip correction factors C from the work of Davies (1945), Fuchs (1964), Allen and Raabe (1982) and this work are summarized in Table 6 for selected Kn values of 0.01, 0.1, 1 and 10. Differences of not more than 0.1% result for the lowest Kn number as expected. However differences of up to 1.8% in C were obtained for larger Kn numbers with the least differences occurring between the values of Davies (1945) and the present work.

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