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CLARENDON PRESS · OXFORD
1976

Oxford University Press, Ely House, London W.1

GLASGOW NEW YORK TORONTO MELBOURNE WELLINGTON
CAPE TOWN IBADAN NAIROBI DAR ES SALAAM LUSAKA ADDIS ABABA
DELHI BOMBAY CALCUTTA MADRAS KARACHI LAHORE DACCA
KUALA LUMPUR SINGAPORE HONG KONG TOKYO

ISBN 0 19 856120 2

PRINTED IN GREAT BRITAIN BY
J. W. ARROWSMITH LTD., BRISTOL, ENGLAND

PREFACE

THIS book is intended primarily for scientists and engineers who wish to analyse practical nonlinear gas flows on the molecular level.

The background material for the analysis is drawn largely from the classical kinetic theory of gases. This is developed from first principles and, unlike conventional treatments, it is based on the point of view that a typical element of gas may not be in thermal equilibrium and generally forms part of a flow field with a non-uniform mass motion. Also, since the formulation of molecular gas flow problems need not necessarily be in terms of the velocity distribution function, the macroscopic gas quantities are initially defined as direct averages of the microscopic molecular quantities. The introduction of the various forms of the velocity distribution function is delayed until they are required for the formulation of the Boltzmann equation. The discussion of this equation leads naturally to the equilibrium state. This state, together with the slightly non-equilibrium state that is described by the Chapman–Enskog theory, provides the key reference quantities. These quantities, which are presented for both simple gases and gas mixtures, are supplemented by a discussion of the gas–surface boundary condition. The aforementioned elementary results are sufficient for the treatment of the collisionless or free molecule flows that are dealt with in Chapter 5.

The material in the first five chapters provides the foundation for the treatment of transition regime flows. This material is supplemented by a set of exercises at the end of each chapter and could provide the basis of a graduate course on molecular gas dynamics. The assumed level of knowledge in mathematics and physics is consistent with the minimum requirements for an engineering or science degree. It is only in the later chapters that it is also assumed that readers have been exposed to an introductory course in continuum gas dynamics.

The Chapman–Enskog theory for the transport properties is not presented in detail because a number of full descriptions are readily available in standard texts. Similarly, in the treatment of transition regime flows, emphasis is placed almost exclusively on nonlinear problems with large perturbations. The reasons for this are that other authors have dealt extensively with small perturbation methods, new problems that are encountered in practice usually involve large perturbations, and one of the major purposes of the book is to provide a detailed description of a numerical method that is better suited to flows with large perturbations. This is the direct simulation Monte Carlo method and, following a general survey of transition regime methods in

Chapter 6, a complete chapter is devoted to an introduction to this method. This includes the description of a representative computer program that is listed in an appendix.

One-dimensional transition regime flows of simple monatomic gases are discussed in Chapter 8, while the final four chapters deal with the progressively more difficult classes of multi-dimensional flows, flows of gas mixtures, polyatomic gas flows, and flows involving chemical reactions. A large number of methods are available for the simple one-dimensional flows, but analysis of the more complex flows becomes increasingly reliant on numerical simulation. The necessary extensions to the direct simulation Monte Carlo method are described in detail and several additional programs are listed in appendices. The chapters on transition regime flow contain a number of new results. Most of these have been obtained from the direct simulation method, but minor extensions have been made to results from other methods and much of the background material is new. The book therefore contains elements of an introductory text on molecular gas dynamics, a handbook on the direct simulation Monte Carlo method, and a research monograph on nonlinear transition regime flows. While this has necessarily led to some compromise, and certainly does not allow an encyclopaedic approach, it is hoped that the various elements have been combined in a way that proves useful to both students and practising engineers and scientists.

ACKNOWLEDGEMENTS

The general arrangement of the introductory material, together with consideration of the possibility of writing a book, had its beginnings in a course given by the author as a Visiting Professor of Aeronautics at the California Institute of Technology in 1969. Thanks are due to Dr. H. P. Liepmann for making this possible. The first drafts of the early chapters were written while Dr. G. S. Springer of the University of Michigan was visiting Sydney and the author is indebted to his valuable suggestions and criticisms.

The development of the direct simulation Monte Carlo method has been supported since its inception by the Air force Office of Scientific Research, United States Air Force, through a series of basic research grants. These have been monitored by Mr. M. Rogers and Mr. P. A. Thurston, whose sustained interest is gratefully acknowledged. Not the least of the benefits of this support is that it has enabled the author to participate in most of the bi-annual International Symposia on rarefied gas dynamics. A number of original results from the method appear in the book; this work has been largely supported by the current grant AFOSR-72-2336. Also, many of the Monte Carlo simulation procedures have come into being as a result of a long period of consultation with TRW Systems Inc. (California). Discussions with Drs. F.

W. Vogenitz and J. E. Broadwell have contributed significantly to these developments.

The typing of the manuscript has been capably handled by Mrs. V. Robinson and Mrs. S. Frost. Drs. D. I. Pullin and A. Chatwani have provided some valuable criticisms of the manuscript. Finally, Mr. T. Tran Cong checked a number of chapters and suggested many detailed improvements to the presentation.

Sydney, Australia *G.A.B.*
June, 1975

LIST OF SYMBOLS

Note: Some symbols, including superscripts and subscripts, that have application only to single problems in Chapter 5 and in Chapters 7–12 have been omitted. This applies also to local changes in the meaning of some listed symbols. FORTRAN variables in the demonstration programs have not been listed.

a	speed of sound
a_c	energy accommodation coefficient, eqn (4.62)
A	a locally specified constant or parameter
$A_2(\eta)$	a definite integral for inverse power law molecules, eqn (4.54)
b	miss distance impact parameter in a binary collision
B	a locally specified constant or parameter
c_p, c_V	specific heats at constant pressure and volume, respectively
c'_m	most probable thermal speed, $c'_m = 1/\beta$
c'_s	root-mean-square thermal speed
$\boldsymbol{c}_0$	stream, mean, or mass velocity, $\boldsymbol{c}_0 = \bar{\boldsymbol{c}}$ for simple gas, eqn (1.37) for gas mixture
$\boldsymbol{c}'$	thermal, peculiar, or random molecular velocity, $\boldsymbol{c}' = \boldsymbol{c} - \boldsymbol{c}_0$
$\boldsymbol{c}_m$	centre of mass velocity of collision pair
$\boldsymbol{c}_r$	relative velocity between two molecules
$\boldsymbol{c}''_p$	velocity defined for species p by $\boldsymbol{c}''_p = \boldsymbol{c}_p - \bar{\boldsymbol{c}}_p$
$\mathrm{d}\boldsymbol{c}$	volume element in velocity space, $\mathrm{d}\boldsymbol{c} = \mathrm{d}u\,\mathrm{d}v\,\mathrm{d}w$
C	a locally specified constant
$\boldsymbol{C}_p$	diffusion velocity of species p, $\boldsymbol{C}_p = \bar{\boldsymbol{c}}_p - \boldsymbol{c}_0$
d	effective or nominal molecular diameter
e_{tr}	specific energy associated with translational modes, eqn (1.21)
e_{int}	specific energy associated with internal modes
$\boldsymbol{e}$	unit vector
E_a	activation energy
E_c	reference energy in collision; total energy in collision
E_t	translational relative energy in collision
f	normalized velocity distribution function in velocity space, eqn (3.1)
f_0	Maxwellian or equilibrium velocity distribution function, eqn (3.46)
f_c	distribution function for molecular speed (subscripts are similarly used to designate the distribution functions for other speeds and velocities)
F	the magnitude of a force; cumulative distribution function
$F^{(N)}$	N particle distribution function, eqn (3.7)
$\boldsymbol{F}$	intermolecular force; external force per unit mass
$\mathscr{F}$	velocity distribution function in phase space, eqn (3.5)

h	Planck's constant, $h = 6{\cdot}6256 \times 10^{-34}$ J s; a linear dimension
H	Boltzmann's H-function, eqn (3.40)
I	molecular moment of inertia
$k(T)$	rate coefficient
k	Boltzmann constant, $k = \mathscr{R}/\mathscr{N} = mR = 1{\cdot}3805 \times 10^{-23}$ J K^{-1}
K	coefficient of heat conduction
(Kn)	Knudsen number, $(Kn) = \lambda/L$
l	linear dimension
l_1	direction cosine with the x-axis
L	linear dimension
m	mass of a single molecule
m_1	direction cosine with the y-axis
m_r	reduced mass, eqn (2.7)
(Ma)	flow Mach number, $(Ma) = c_0/a$
$(Ma)_s$	shock Mach number
$\mathscr{M}$	molecular weight
n	number density
n_0	Loschmidt's number, $n_0 = 2{\cdot}68699 \times 10^{19}$ cm^{-3}
n_1	direction cosine with the z axis
N	number of molecules; number flux of molecules
N_c	number of collisions
$\mathscr{N}$	Avogadro's number, $\mathscr{N} = 6.0225 \times 10^{23}$ mol^{-1}
p	pressure, eqn (1.19); normal momentum flux per unit area
p_{xy}	component of $\boldsymbol{P}$ based on the flux of x momentum in the y direction (similarly for other components)
P	probability
$\mathbf{p}$	pressure tensor, eqn (1.17)
(Pr)	Prandtl Number
q_x	component of q in the x direction
$\boldsymbol{q}$	heat flux vector, eqn (1.27)
Q	physical quantity associated with a molecule
Q^a, Q^{aa}	partition functions
r	radius; radial coordinate
$\boldsymbol{r}$	position vector
$\mathrm{d}\boldsymbol{r}$	volume element in physical space, $\mathrm{d}\boldsymbol{r} = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$
R	gas constant, $R = \mathscr{R}/\mathscr{M}$
R_f	random fraction
$\mathscr{R}$	universal gas constant, $\mathscr{R} = 8{\cdot}3143$ J mol^{-1} K^{-1}
s	molecular speed ratio, $s = U\beta$; distance; number of species in a gas mixture; number of square terms
S	entropy; area
t	time
t_f	energy transfer factor in energy sink model

T	thermodynamic temperature
T_{tr}	translational kinetic temperature, eqn (1.23)
T_{int}	kinetic temperature of internal modes, eqn (1.25)
T_{ov}	overall kinetic temperature, eqn (1.26)
u	velocity component in the x direction
U	speed
v	velocity components in the y direction
V	volume in physical space
w	velocity component in the z direction
W	dimensionless impact parameter, $W = b/r$.
W_f	weighting factor
W_0	dimensionless impact parameter for inverse power law molecules, eqn (2.24)
$W_{0,m}$	cut-off value of W_0
x	Cartesian coordinate axis in physical space, dummy variable
y	Cartesian coordinate axis in physical space
z	Cartesian coordinate axis in physical space
α	angle of incidence, angle, degree of dissociation
β	reciprocal of most probable molecular speed in an equilibrium gas, $\beta = (2RT)^{-\frac{1}{2}}$
γ	ratio of specific heats, $\gamma = c_p/c_V$
Γ	mass flux; gamma function
δ	average spacing between molecules, $\delta = n^{-\frac{1}{3}}$
$\Delta[Q]$	collision integral, eqn (3.26)
ε	azimuth angle impact parameter in binary collision; fraction of molecules specularly reflected at a surface; symmetry factor
ε_{int}	internal energy of a single molecule
ε_0	parameter in Chapman–Enskog expansion, eqn (3.50)
ζ	number of internal degrees of freedom
η	exponent of inverse power law molecular force, eqn (2.23); temperature exponent in generalized Arrhenius equation
θ	angular coordinate
θ_A	angle between apse line and relative velocity vector
κ	constant in inverse power law molecular force, eqn (2.23)
λ	mean free path, eqn (1.8)
λ_0	mean free path in equilibrium gas, eqn (4.38)
μ	coefficient of viscosity
ν	collision frequency, eqn (1.6)
ν_0	collision frequency in an equilibrium gas, eqn (4.36)
$\sigma\, d\Omega$	differential cross-section, eqn (2.11)
σ_T	total collision cross-section, eqn (2.14)
σ_R	reactive cross-section
τ	shear stress; mean collision time
τ_{xy}	viscous stress in the plane normal to x and in the y direction

τ	viscous stress tensor, eqn (1.20)
ϕ	intermolecular potential; azimuth angle
Φ	dissipation function, eqn (3.37); parameter in alternate Chapman–Enskog expansion, eqn (3.51)
χ	deflection angle of the relative velocity vector in a collision
ω_m	most probable angular speed of a molecule in an equilibrium gas
ω	angular velocity
Ω	solid angle

Superscripts and subscripts

Note: The subscripts in the above list do not, in general, conform to the following meanings.

*	post-collision value; sonic conditions
1, 2	particular molecules or molecular classes
p, q	particular molecular species
c	continuum value
f	free molecule or collisionless value
i	incident; intial; inward
r	reflected; relative
∞	freestream value
w	value at a surface
x, y, z	components in the x, y, and z directions, respectively

CONTENTS

1

THE MOLECULAR MODEL

1.1 Introduction

A GAS flow may be modelled on either a macroscopic or a microscopic level. The macroscopic model regards the gas as a continuum and the description is in terms of the variations of the macroscopic velocity, density, pressure, and temperature with distance and time. On the other hand, the microscopic or molecular model recognizes the particulate structure of a gas as a myriad of discrete molecules and ideally provides information on the position and velocity of every molecule at all times. However, a description in such detail is rarely, if ever, practical and a gas flow is almost invariably described in terms of macroscopic quantities. The two models must therefore be distinguished by the approach through which the description is obtained, rather than by the nature of the description itself. This book is concerned with the microscopic or molecular approach and the first question which must be answered is whether this approach can solve problems that could not be solved through the conventional continuum approach.

The macroscopic quantities at any point in a flow may be identified with average values of appropriate molecular quantities; the averages being taken over the molecules in the vicinity of the point. The continuum description is valid as long as the smallest significant volume in the flow contains a sufficient number of molecules to establish meaningful averages. The existence of a formal link between the macroscopic and microscopic quantities means that the equations which express the conservation of mass, momentum, and energy in the flow may be derived from either approach. While this might suggest that neither of the approaches can provide information that is not also accessible to the other, it must be remembered that the conservation equations do not form a determinate set unless the shear stresses and heat flux can be expressed in terms of the other macroscopic quantities. It is the failure to meet this requirement, rather than the breakdown of the continuum description, that places a limit on the range of validity of the continuum equations. More specifically, the Navier–Stokes equations of continuum gas dynamics fail when gradients of the macroscopic variables become so steep that their scale length is of the same order as the average distance travelled by the molecules between collisions, or *mean free path*. A less precise but more convenient parameter is obtained if the scale length of the gradients is replaced by a characteristic dimension of the

flow. The ratio of the mean free path λ to the characteristic dimension L defines the *Knudsen number* (Kn) i.e.

$$(Kn) = \lambda/L. \tag{1.1}$$

The necessary condition for the validity of the continuum approach is, therefore, that the Knudsen number be small compared with unity.

There appears to be no alternative to the molecular approach when the Knudsen number is of order unity or higher. A high Knudsen number may result from either a large mean free path or a very small characteristic dimension. The former is usually the case and, since the mean free path in a given gas is inversely proportional to the density, it is a consequence of a very low density. Hence the title 'rarefied gas dynamics' that is very frequently applied to the subject of this book. Typical applications in this category include internal flows in vacuum systems and aerodynymics in the outer atmosphere. However, it must be kept in mind that the alternative requirement of a small characteristic dimension can be met at any density. For example, the molecular approach is required for the study of the forces on sufficiently small particles suspended in the atmosphere, the internal structure of shock waves, and the propagation of sound at extremely high frequencies.

Having defined the conditions in which the molecular approach must be used, we must also consider whether there are any circumstances in which it is to be preferred over the continuum approach when both provide valid formulations. This possibility has generally been completely dismissed on account of the overwhelming difficulties associated with formal analytical solutions of the conventional microscopic equations. However, even with the continuum formulation, exact or approximate analytical solutions can only be obtained for comparatively simple flows. Numerical solutions are required for practical problems involving large disturbances and complex boundary conditions. Massive computer calculations are becoming increasingly important in gas dynamics and, for such calculations, the molecular approach will be shown to sometimes offer advantages over the continuum approach.

1.2. The simple dilute gas

The basic quantities associated with the molecular model are the number of molecules per unit volume and the mass, size, and velocity of each molecule. These quantities must be related to the mean free path and collision frequency in order to establish the distance and time scales of the effects due to the collisional interactions among the molecules. Also, since the results from the molecular approach will generally be presented in terms of the macroscopic quantities, we must establish the formal relationships between the macroscopic and microscopic quantities. For reasons of simplicity and clarity, the

discussion in this section will be restricted to a gas consisting of a single chemical species in which all the molecules are assumed to have the same structure. Such a gas is called a *simple gas.*

The number of molecules in one mole of gas is a fundamental physical constant called *Avogadro's number* $\mathcal{N}$. Avogadro's law also states that the volume occupied by a mole of any gas at a particular temperature and pressure is a constant. The number of molecules per unit volume, or *number density* n, of a gas therefore depends on the temperature and pressure, but is independent of the composition of the gas. The *mass* m of a single molecule is obtained by dividing the *molecular weight* $\mathcal{M}$ of the gas by Avogadro's number, i.e.

$$m = \mathcal{M}/\mathcal{N} \tag{1.2}$$

The average volume available to a molecule is $1/n$, so the mean molecular spacing δ is given by

$$\delta = n^{-\frac{1}{3}}. \tag{1.3}$$

The ideal molecular structure, from the point of view of the theoretician, would be a hard elastic sphere of diameter d. Then, as shown in Fig. 1.1,

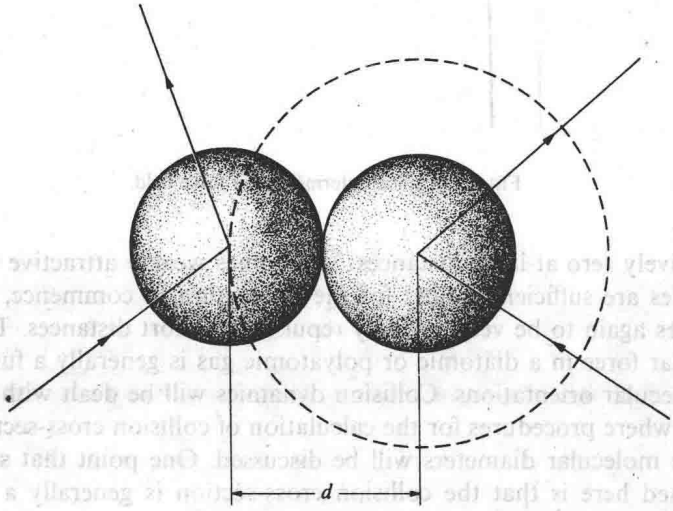

FIG. 1.1. Collision between two hard spheres of diameter d.

two molecules collide if their trajectories are such that the distance between their centres decreases to d. The *total collision cross-section* for these molecules is, therefore,

$$\sigma_T = \pi d^2. \tag{1.4}$$

A real molecule comprises one or more atoms, each consisting of a nucleus surrounded by orbiting electrons. Molecular size is a quantity that cannot be precisely and uniquely defined. However, the effect of a close encounter between molecules can be calculated from a knowledge of the intermolecular force field. The general form of the force field between two neutral molecules is shown in Fig. 1.2 as a function of the distance between them. The force

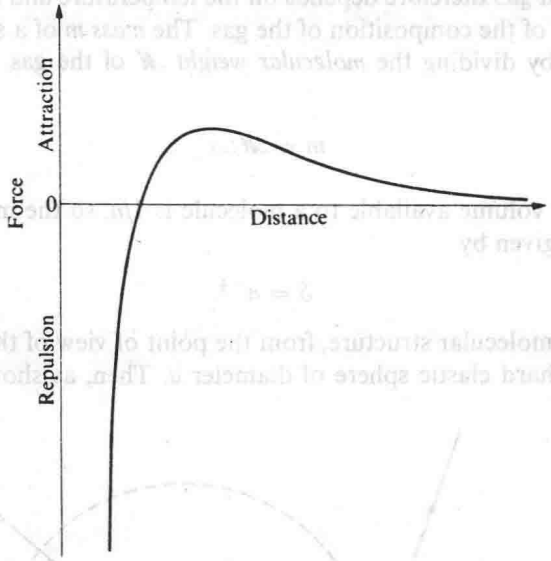

FIG. 1.2. Typical intermolecular force field.

is effectively zero at large distances; it becomes weakly attractive when the molecules are sufficiently close for the interaction to commence, but then decreases again to be very strongly repulsive at short distances. The intermolecular force in a diatomic or polyatomic gas is generally a function of the molecular orientations. Collision dynamics will be dealt with in detail in § 2.2 where procedures for the calculation of collision cross-sections and effective molecular diameters will be discussed. One point that should be mentioned here is that the collision cross-section is generally a function of the relative speed between the collision partners.

The proportion of the space occupied by a gas that actually contains a molecule is of the order of $(d/\delta)^3$. Eqn (1.3) shows that, for sufficiently low densities, the molecular spacing δ is large compared with the effective molecular diameter d. Under these circumstances, only an extremely small proportion of space is occupied by molecules and each molecule will, for the most part, be moving freely in space outside the range of influence of