

# **Progress in Mathematical Physics**

Volume 41

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Carlo Cercignani

# **Slow Rarefied Flows**

Theory and Application to  
Micro-Electro-Mechanical Systems

Birkhäuser Verlag  
Basel • Boston • Berlin

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2000 Mathematics Subject Classification 82B40, 82C40

A CIP catalogue record for this book is available from the Library of Congress, Washington D.C., USA

Bibliographic information published by Die Deutsche Bibliothek  
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <http://dnb.ddb.de>.

**ISBN 3-7643-7534-5 Birkhäuser Verlag, Basel – Boston – Berlin**

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Part of Springer Science+Business Media

Printed on acid-free paper produced of chlorine-free pulp. TCF ∞

Printed in Germany

ISBN-10: 3-7643-7534-5

e-ISBN: 3-7643-7537-X

ISBN-13: 987-3-7643-7534-8

9 8 7 6 5 4 3 2 1

[www.birkhauser.ch](http://www.birkhauser.ch)

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# Preface

This volume is intended to cover the present status of the mathematical tools used to deal with problems related to slow rarefied flows. The meaning and usefulness of the subject, and the extent to which it is covered in the book, are discussed in some detail in the introduction. In short, I tried to present the basic concepts and the techniques used in probing mathematical questions and problems which arise when studying slow rarefied flows in environmental sciences and micromachines. For the book to be up-to-date without being excessively large, it was necessary to omit some topics, which are treated elsewhere, as indicated in the introduction and, whenever the need arises, in the various chapters of this volume. Their omission does not alter the aim of the book, to provide an understanding of the essential mathematical tools required to deal with slow rarefied flows and give the background for a study of the original literature.

Although I have tried to give a rather complete bibliographical coverage, the choice of the topics and of the references certainly reflects a personal bias and I apologize in advance for any omission.

I wish to thank Lorenzo Valdettaro, Antonella Abbà, Silva Lorenzani and Paolo Barbante for their help with pictures and especially Professor Ching Shen for his permission to reproduce his pictures on microchannel flows.

*Milano, December 2005*

Carlo Cercignani

# Introduction

Rarefied gas dynamics can be defined as the study of gas flows in which the average value of the distance between two subsequent collisions of a molecule (the so-called mean free path) is not negligible in comparison with a length typical of the structure of the flow being considered, e.g., the thickness of a microchannel or the radius of curvature of the nose of a space shuttle. Thus it intrinsically requires the use of statistical ideas typical of the kinetic theory of gases as embodied in the integro-differential equation proposed by Boltzmann in 1872 and bearing his name.

Rarefied gas dynamics has existed, in principle, since the 19th century, but came in the foreground with space exploration. One can even give a birthdate, July 1958, when the first international symposium on rarefied gas dynamics was held in Nice (France). Since then, these symposia have been held regularly every second year. When glancing through the corresponding proceedings, one should not be surprised to find a shift of topics. The first few volumes contain a considerable amount of experimental papers and the theoretical papers contain very general surveys on the Boltzmann equation that rules the evolution of rarefied flows, but very few papers dealing with explicit solutions of some elementary problems. The first numerical solutions of some interest appear in 1962, but still in the late 1960s were few in number and not so accurate. Then one witnesses the reduction of experimental work and the increasing importance of numerical simulation. In the most recent volumes, experiments occupy just a few pages of the proceedings. This is compensated for by the fact that numerical simulations have spread through all the subfields, indicating the maturity reached by the theoretical understanding of the subject. Increasingly complicated phenomena, such as reacting flows or evaporation and condensation, are the object of widespread interest.

The mathematical theory of the Boltzmann equation goes back to such illustrious mathematicians as Hilbert and Carleman and is mentioned in the motivation of the Fields medal awarded to P.L. Lions in 1994. Some details of this theory will be presented in this book. The present introduction is mainly devoted to explain why this equation is so important for applications. We also remark that this book, although describing a well-defined topic, can serve two sets of readers: those more interested in the basic mathematical theory and those more interested

in applications. The former might restrict themselves to Chapters 1–4, the latter to Chapter 1, the first section of Chapter 4 and Chapters 5–7.

In addition to space research, rarefied gas dynamics is also required in the area of environmental problems. Understanding and controlling the formation, motion, reactions and evolution of particles of varying composition and shapes, ranging from a diameter of the order of  $.001 \mu\text{m}$  to  $50 \mu\text{m}$ , as well as their space-time distribution under gradients of concentration, pressure, temperature and the action of radiation, has grown in importance, because of the increasing awareness of the local and global problems related to the emission of particles from electric power plants, chemical plants, vehicles as well as of the role played by small particles in the formation of fog and clouds, in the release of radioactivity from nuclear reactor accidents, and in the problems arising from the exhaust streams of aerosol reactors, such as those used to produce optical fibers, catalysts, ceramics, silicon chips and carbon whiskers.

One cubic centimeter of atmospheric air at ground level contains approximately  $2.5 \times 10^{19}$  molecules. About a thousand of them may be charged (ions). A typical molecular diameter is  $3 \times 10^{-10} \text{ m}$  ( $3 \times 10^{-4} \mu\text{m}$ ) and the average distance between the molecules is about ten times as much. The mean free path is of the order of  $10^{-8} \text{ m}$ , or  $10^{-2} \mu\text{m}$ . In addition to molecules and ions, one cubic centimeter of air also contains a significant number of particles varying in size, as indicated above. In relatively clean air, the number of these particles can be  $10^5$  or more, including pollen, bacteria, dust, and industrial emissions. They can be both beneficial and detrimental, and arise from a number of natural sources as well as from the activities of all living organisms, especially humans. The particles can have complex chemical compositions and shapes, and may even be toxic or radioactive. A suspension of particles in a gas is known as an aerosol. Atmospheric aerosols are of global interest and have important impact on our lives. Aerosols are also of great interest in numerous scientific and engineering applications.

A third area of application of rarefied gas dynamics has emerged in the last few years and will be discussed in detail in the last chapter of the present book. Small size machines, called micromachines, are being designed and built. Their typical sizes range from a few microns to a few millimeters. Rarefied flow phenomena that are more or less laboratory curiosities in machines of more usual size can form the basis of important systems in the micromechanical domain. In fact, rarefied gas flows occur in many micro-electro-mechanical systems (MEMS), such as actuators, microturbines, gas chromatographs, and micro air vehicles (MAVs). A correct prediction of these flows is important to design and develop MEMS. Nanoscale design occurs for computer components as well and is no longer limited to chip technology but extends to mechanical devices as well. In a modern disk drive, the read/write head floats at distances of the order of  $50 \text{ nm}$  above the surface of the spinning platter. The prediction of the vertical force on the head (as obtained from the pressure distribution in the gas) is a crucial design calculation since the head will not accurately read or write if it flies too high. If the head flies too low, it can catastrophically collide against the platter. Micro-channels

may have further computer applications because they are supposed to dissipate the heat generated in microchips more effectively than fans, and may be used as a more practical cooling system in integrated circuit chips.

Since, as these examples indicate, micro-devices are gaining popularity both in commercial applications and in scientific research, there exists a rapidly growing interest in improving the conventional design techniques related with these devices. Micro-devices are often operated in gaseous environments (typically air), and thus their performances are affected by the gas around them. The numerical simulation of all these flows cannot be performed with the Navier–Stokes equations (or the related Reynolds equation for a slider air bearing) because the smallest characteristic length of MEMS or of the thin air film occurring in a computer drive is comparable with (or smaller than) the mean free path of the gas molecules. For this reason the continuum equations are no longer valid and the Boltzmann equation must be invoked to understand and compute the rarefied flows related to these devices.

Numerical methods based on this equation are generally numerically expensive especially when the flow to be considered progresses from free molecular, through transitional, to continuum regions. Since these flows, contrary to the flow past space vehicles, are usually at low Mach number, the use of the linearized Boltzmann equation is permissible and this revives old methods developed in the sixties and seventies of the 20th century to deal with this equation.

Among the rarefied flows of interest, one should not forget the design and simulation of the aerosol reactors, used to produce optical fibers, catalysts, ceramics, silicon chips and carbon whiskers, which have been mentioned above as sources of air pollution. A further area of interest occurs in the vacuum industry. Although this area has existed for a long time, the expense of the early computations with kinetic theory precluded applications of numerical methods. The latter could develop only in the context of the aerospace industry, because the big budgets required till recently were available only there.

The present volume is an attempt to cover the mathematical results and techniques to deal with rarefied flows when the speeds are small with respect to the sound speed. The mathematical theory is much more advanced in this case and provides a rigorous justification for the use of the linearized Boltzmann equation, which avoids costly simulations based on Monte Carlo methods.

After introducing the Boltzmann equation in Chapter 1, we shall survey the rigorous theorems on validity and existence in Chapter 2. Chapter 3 is devoted to the basic existence theory for flows close to equilibria in an infinite expanse of gas or in a periodic box. Chapter 4 deals with more realistic boundary conditions and Chapter 5 deals with the techniques used to solve problems in the simple but extremely important case of a slab geometry. Chapter 6 discusses problems in three dimensions and Chapter 7 is devoted to the recent contributions to rarefied lubrication theory with particular attention to applications to MEMS.

# Chapter 1

## The Boltzmann Equation

### 1.1 Historical Introduction

In 1738 Daniel Bernoulli advanced the idea that gases are formed of elastic molecules rushing hither and thither at large speeds, colliding and rebounding according to the laws of elementary mechanics. Of course, this was not a completely new idea, because several Greek philosophers asserted that the molecules of all bodies are in motion even when the body itself appears to be at rest. The new idea was that the mechanical effect of the impact of these moving molecules when they strike against a solid is what is commonly called the pressure of the gas. In fact if we were guided solely by the atomic hypothesis, we might suppose that the pressure would be produced by the repulsions of the molecules. Although Bernoulli's scheme was able to account for the elementary properties of gases (compressibility, tendency to expand, rise of temperature in a compression and fall in an expansion, trend toward uniformity), no definitive opinion could be passed on it until it was investigated quantitatively. The actual development of the kinetic theory of gases was, accordingly, accomplished much later, in the nineteenth century.

Frequently the molecules of a gas can be assumed to be perfectly elastic spheres that move according to the laws of classical mechanics. Thus, e.g., if no external force, such as gravity, is assumed to act on the molecules, each of them will move in a straight line unless it happens to strike another sphere or a solid wall. Systems of this kind are usually called billiards, for obvious reasons.

Although the rules generating the dynamics of these systems are easy to prescribe, the phenomena associated with this dynamics are not so simple. They are actually rather difficult to understand, especially if one is interested in the asymptotic behavior of the system for long times (ergodic properties) or in the case when the number of spheres is very large (kinetic and hydrodynamical limits). Both aspects of the dynamics of hard spheres are relevant when dealing with a gas,

but we shall now concentrate upon the problem of outlining the behavior of this system when the number of the particles is very large. This is due to the fact that there are about  $2.7 \cdot 10^{19}$  molecules in a cubic centimeter of a gas at atmospheric pressure and a temperature of  $0^\circ\text{C}$ .

Given the enormous number of particles to be considered, it would of course be a perfectly hopeless task to attempt to describe the state of the gas by specifying the so-called microscopic state, i.e., the position and velocity of every individual particle, and we must have recourse to statistics. This is possible because in practice all that our observation can detect are changes in the macroscopic state of the gas, described by quantities such as density, velocity, temperature, stresses, heat flow, which are related to the suitable averages of quantities depending on the microscopic state.

In 1866 James Clerk Maxwell (1831–1879) developed an accurate method<sup>24</sup>, based on the so-called transfer equations, and discovered the particularly simple properties of a model, according to which the molecules interact at a distance with a force inversely proportional to the fifth power of the distance (nowadays commonly called Maxwellian molecules). In the same paper he gave a justification of his earlier formula for the velocity distribution function for a gas in equilibrium.

With his transfer equations, Maxwell had come very close to an evolution equation for the distribution, but this step<sup>4</sup> must be credited to Ludwig Boltzmann (1844–1906). The equation under consideration is usually called the Boltzmann equation and sometimes the Maxwell–Boltzmann equation (to recognize the important role played by Maxwell in its discovery).

In the same paper, where he gave a heuristic derivation of his equation, Boltzmann deduced an important consequence from it, which later came to be known as the *H*-theorem. This theorem attempts to explain the irreversibility of natural processes in a gas, by showing how molecular collisions tend to increase entropy. The theory was attacked by several physicists and mathematicians in the 1890s, because it appeared to produce paradoxical results. However, within a few years of Boltzmann's suicide in 1906, the existence of atoms had been firmly established by experiments such as those on Brownian motion.

The paradoxes indicate, however, that some reinterpretation is necessary. Boltzmann himself had proposed that the *H*-theorem be interpreted statistically; later, Paulus Ehrenfest (1880–1933), together with his wife Tatiana, gave a brilliant analysis of the matter, which elucidated Boltzmann's ideas and made it highly plausible, at least from a heuristic standpoint. A rigorous analysis, however, had still to come.

In the meantime, the Boltzmann equation had become a practical tool for investigating the properties of dilute gases. In 1912 the great mathematician David Hilbert (1862–1943) indicated<sup>19</sup> how to obtain approximate solutions of the Boltzmann equation by a series expansion in a parameter, inversely proportional to the gas density. The paper is also reproduced as Chapter XXII of his treatise entitled *Grundzüge einer allgemeinen Theorie der linearen Integralgleichungen*. The reasons for this are clearly stated in the preface of the book (“Neu hinzugefügt habe

ich zum Schluss ein Kapitel über kinetische Gastheorie. [...] erblicke ich in der Gastheorie die glänzendste Anwendung der die Auflösung der Integralgleichungen betreffenden Theoreme”).

In about the same year (1916–1917) Sidney Chapman<sup>12</sup> (1888–1970) in England and David Enskog<sup>14</sup> (1884–1947) in Sweden independently obtained approximate solutions of the Boltzmann equation, valid for a sufficiently dense gas. The results were identical as far as practical applications were concerned, but the methods differed widely in spirit and detail. Enskog presented a systematic technique generalizing Hilbert’s idea, while Chapman simply extended a method previously indicated by Maxwell to obtain transport coefficients. Enskog’s method was adopted by S. Chapman and T. G. Cowling in their book *The Mathematical Theory of Non-uniform Gases* and thus became to be known as the Chapman–Enskog method.

Then for many years no essential progress in solving the equation came. Rather the ideas of kinetic theory found their way in other fields, such as radiative transfer, the theory of ionized gases and, subsequently, in the theory of neutron transport. Almost unnoticed, however, the rigorous theory of the Boltzmann equation had started in 1933 with a paper<sup>5</sup> by Tage Gillis Torsten Carleman (1892–1949), who proved a theorem of global existence and uniqueness for a gas of hard spheres in the so-called space homogeneous case. The theorem was proved under the restrictive assumption that the initial data depend upon the molecular velocity only through its magnitude. This restriction is removed in a posthumous book by the same author<sup>6</sup>.

In 1949 Harold Grad (1923–1986) wrote a paper<sup>17</sup>, which became widely known because it contained a systematic method of solving the Boltzmann equation by expanding the solution into a series of orthogonal polynomials. In the same paper, however, Grad made a more basic contribution to the theory of the Boltzmann equation for molecules of diameter  $\sigma$ . In fact, he formulated a conjecture on the validity of the Boltzmann equation. In his words: “From the preceding discussion it is possible to see along what lines a rigorous derivation of the Boltzmann equation should proceed. First, from equilibrium considerations we must let the number density of molecules,  $N$ , increase without bound. At the same time we would like the macroscopic properties of the gas to be unchanged. To do this we allow  $m$  to approach zero in such a way that  $mN = \rho$  is fixed. The Boltzmann equation for elastic spheres, (2.37) has a factor  $\sigma^2/m$  in the collision term. If  $\sigma$  is made to approach to zero at such a rate that  $\sigma^2/m$  is fixed, then the Boltzmann equation remains unaltered. [...] In the limiting process described here, it seems likely that solutions of Liouville’s equation attain many of the significant properties of the Boltzmann equation.”

In the 1950s there were some significant results concerning the Boltzmann equation. A few exact solutions were obtained by C. Truesdell<sup>28</sup> in the U.S.A. and by V. S. Galkin<sup>15,16</sup> in the Soviet Union, while the existence theory was extended by D. Morgenstern<sup>25</sup>, who proved a global existence theorem for a gas of Maxwellian molecules in the space homogeneous case. His work was extended

by L. Arkeryd<sup>1,2</sup> in 1972.

In the 1960s, under the impact of the problems related to space research, the main interest was in the direction of finding approximate solutions of the Boltzmann equation and developing mathematical results for the perturbation of equilibrium<sup>7,8</sup>. Important methods developed by H. Grad<sup>18</sup> were brought to completion much later by S. Ukai, Y. Shizuta, K. Asano, T. Nishida and K. Imai<sup>26,27,29</sup>.

The problem of proving the validity of the Boltzmann equation was still completely open. In 1972, C. Cercignani<sup>9</sup> proved that taking the limit indicated by Grad in the passage quoted above (now currently called the Boltzmann–Grad limit) produced, from a formal point of view, a perfectly consistent theory, i.e., the so-called Boltzmann hierarchy. This result clearly indicated that the difficulties of the rigorous derivation of the Boltzmann equation were not of a formal nature but were at least of the same order of difficulty as those of proving theorems of existence and uniqueness in the space inhomogeneous case. Subsequently, O. Lanford proved<sup>23</sup> that the formal derivation becomes rigorous if one limits himself to a sufficiently short time interval. The problem of a rigorous, globally valid justification of the Boltzmann equation is still open, except for the case of an expanding rare cloud of gas in a vacuum, for which the difficulties were overcome by R. Illner and M. Pulvirenti<sup>20,21</sup>, after Illner and Shinbrot had provided the corresponding existence and uniqueness theorem for the Boltzmann equation<sup>22</sup>.

More recently, R. Di Perna and P. L. Lions<sup>13</sup> have proved a global existence theorem for quite general data, but several important problems, such as proving that energy is conserved or controlling the growth of density are still open.

## 1.2 The Boltzmann Equation

The phenomena associated with the dynamics of molecules are not so simple, especially because the number of molecules usually considered is extremely large: there are about  $2.7 \cdot 10^{19}$  in a cubic centimeter of a gas at atmospheric pressure and a temperature of  $0^\circ\text{C}$ .

Given the vast number of particles to be considered, it would of course be a hopeless task to attempt to describe the state of the gas by specifying the so-called microscopic state, i.e., the position and velocity of every individual sphere; we must have recourse to statistics. A description of this kind is made possible because in practice all that our typical observations can detect are changes in the macroscopic state of the gas, described by quantities such as density, bulk velocity, temperature stresses, heat flow, which are related to some suitable averages of quantities depending on the microscopic state.

The exact dynamics of  $N$  particles is a useful conceptual tool, but cannot in any way be used in practical calculations because it requires a huge number of real variables (of the order of  $10^{20}$ ). This was realized by Maxwell and Boltzmann when they started to work with the one-particle probability density, or distribution function  $P^{(1)}(\mathbf{x}, \boldsymbol{\xi}, t)$ . The latter is a function of seven variables, i.e., the compo-

nents of the two vectors  $\mathbf{x}$  and  $\boldsymbol{\xi}$  and time  $t$ . In particular, Boltzmann wrote an evolution equation for  $P^{(1)}$  by means of a heuristic argument, which we shall try to present in such a way as to show where extra assumptions are introduced.

Let us first consider the meaning of  $P^{(1)}(\mathbf{x}, \boldsymbol{\xi}, t)$ ; it gives the probability density of finding one fixed particle (say, the one labelled by 1) at a certain point  $(\mathbf{x}, \boldsymbol{\xi})$  of the six-dimensional reduced phase space associated with the position and velocity of that molecule. In order to simplify the treatment, we shall for the moment assume that the molecules are hard spheres, whose center has position  $\mathbf{x}$ . When the molecules collide, momentum and kinetic energy must be conserved; thus the velocities after the impact,  $\boldsymbol{\xi}'_1$  and  $\boldsymbol{\xi}'_2$ , are related to those before the impact,  $\boldsymbol{\xi}_1$  and  $\boldsymbol{\xi}_2$ , by

$$\begin{aligned}\boldsymbol{\xi}'_1 &= \boldsymbol{\xi}_1 - \mathbf{n}[\mathbf{n} \cdot (\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2)], \\ \boldsymbol{\xi}'_2 &= \boldsymbol{\xi}_2 + \mathbf{n}[\mathbf{n} \cdot (\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2)]\end{aligned}\tag{1.2.1}$$

where  $\mathbf{n}$  is the unit vector along  $\boldsymbol{\xi}_1 - \boldsymbol{\xi}'_1$ . Note that the relative velocity

$$\mathbf{V} = \boldsymbol{\xi}_1 - \boldsymbol{\xi}_2\tag{1.2.2}$$

satisfies

$$\mathbf{V}' = \mathbf{V} - 2\mathbf{n}(\mathbf{n} \cdot \mathbf{V})\tag{1.2.3}$$

i.e., undergoes a specular reflection at the impact. This means that if we split  $\mathbf{V}$  at the point of impact into a normal component  $\mathbf{V}_n$ , directed along  $\mathbf{n}$  and a tangential component  $\mathbf{V}_t$  (in the plane normal to  $\mathbf{n}$ ), then  $\mathbf{V}_n$  changes sign and  $\mathbf{V}_t$  remains unchanged in a collision. We can also say that  $\mathbf{n}$  bisects the directions of  $\mathbf{V}$  and  $-\mathbf{V}' = -(\boldsymbol{\xi}'_1 - \boldsymbol{\xi}'_2)$  (see Fig. 1.1).

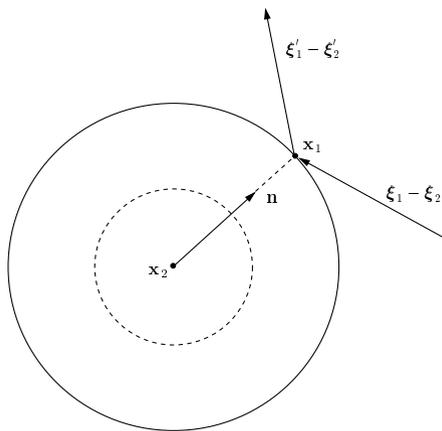


Figure 1.1: The directions of the relative velocities before and after the impact are bisected by the unit vector  $\mathbf{n}$ .

Let us remark that, in the absence of collisions,  $P^{(1)}$  would remain unchanged along the trajectory of a particle and would satisfy

$$\frac{\partial P^{(1)}}{\partial t} + \boldsymbol{\xi}_1 \cdot \frac{\partial P^{(1)}}{\partial \mathbf{x}_1} + \mathbf{X}_1 \cdot \frac{\partial P^{(1)}}{\partial \boldsymbol{\xi}_1} = 0$$

where  $\mathbf{X}_1$  is any external force per unit mass, such as gravity, acting on the molecule, which will be neglected in the rest of the book.

We must now evaluate the effects of collisions on the time evolution of  $P^{(1)}$ . Note that the probability of occurrence of a collision is related to the probability of finding another molecule with a center at exactly one diameter from the center of the first one, whose distribution function is  $P^{(1)}$ . Thus, generally speaking, in order to write the evolution equation for  $P^{(1)}$  we shall need another function,  $P^{(2)}$ , which gives the probability density of finding, at time  $t$ , the first molecule at  $\mathbf{x}_1$  with velocity  $\boldsymbol{\xi}_1$  and the second at  $\mathbf{x}_2$  with velocity  $\boldsymbol{\xi}_2$ ; obviously  $P^{(2)} = P^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2, t)$ . Hence  $P^{(1)}$  satisfies an equation of the form

$$\frac{\partial P^{(1)}}{\partial t} + \boldsymbol{\xi}_1 \cdot \frac{\partial P^{(1)}}{\partial \mathbf{x}_1} = G - L. \quad (1.2.4)$$

Here  $L d\mathbf{x}_1 d\boldsymbol{\xi}_1 dt$  gives the expected number of particles with position between  $\mathbf{x}_1$  and  $\mathbf{x}_1 + d\mathbf{x}_1$  and velocity between  $\boldsymbol{\xi}_1$  and  $\boldsymbol{\xi}_1 + d\boldsymbol{\xi}_1$  which disappear from these ranges of values because of a collision in the time interval between  $t$  and  $t + dt$ , and  $G d\mathbf{x}_1 d\boldsymbol{\xi}_1 dt$  gives the analogous number of particles entering the same range in the same time interval. The count of these numbers is easy, provided we use the trick of imagining particle 1 as a sphere at rest and endowed with twice the actual diameter  $\sigma$  and the other particles to be point masses with velocity  $(\boldsymbol{\xi}_i - \boldsymbol{\xi}_1) = \mathbf{V}_i$ . In fact, each collision will send particle 1 out of the above range and the number of the collisions of particle 1 will be the number of expected collisions of any other particle with that sphere. Since there are exactly  $(N - 1)$  identical point masses and multiple collisions can be disregarded (because they form a set of measure zero in the set of collisions),  $G = (N - 1)g$  and  $L = (N - 1)l$ , where the lower case letters indicate the contribution of a fixed particle, say particle 2. We shall then compute the effect of the collisions of particle 2 with particle 1. Let  $\mathbf{x}_2$  be a point of the sphere such that the vector joining the center of the sphere with  $\mathbf{x}_2$  is  $\sigma \mathbf{n}$ , where  $\mathbf{n}$  is a unit vector. A cylinder with height  $|\mathbf{V} \cdot \mathbf{n}| dt$  (where we write just  $\mathbf{V}$  for  $\mathbf{V}_2$ ) and base area  $dS = \sigma^2 d\mathbf{n}$  (where  $d\mathbf{n}$  is the area of a surface element of the unit sphere about  $\mathbf{n}$ ) will contain the particles with velocity  $\boldsymbol{\xi}_2$  hitting the base  $dS$  in the time interval  $(t, t + dt)$  (see Fig. 1.2); its volume is  $\sigma^2 d\mathbf{n} |\mathbf{V} \cdot \mathbf{n}| dt$ . Thus the number of collisions of particle 2 with particle 1 in the ranges  $(\mathbf{x}_1, \mathbf{x}_1 + d\mathbf{x}_1)$ ,  $(\boldsymbol{\xi}_1, \boldsymbol{\xi}_1 + d\boldsymbol{\xi}_1)$ ,  $(\mathbf{x}_2, \mathbf{x}_2 + d\mathbf{x}_2)$ ,  $(\boldsymbol{\xi}_2, \boldsymbol{\xi}_2 + d\boldsymbol{\xi}_2)$ ,  $(t, t + dt)$  occurring at points of  $dS$  is  $P^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2, t) d\mathbf{x}_1 d\boldsymbol{\xi}_1 d\boldsymbol{\xi}_2 x \sigma^2 d\mathbf{n} |\mathbf{V} \cdot \mathbf{n}| dt$ . If we want the number of collisions of particle 1 with 2, when the range of the former is fixed but the latter may have any velocity  $\boldsymbol{\xi}_2$  and any position  $\mathbf{x}_2$  on the sphere (i.e., any  $\mathbf{n}$ ), we integrate over the sphere and all the possible velocities of particle 2 to obtain:

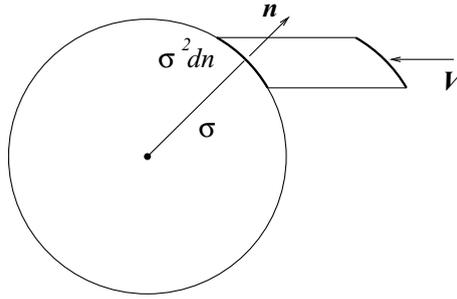


Figure 1.2: Calculation of the number of collisions between two molecules.

$$ld\mathbf{x}_1 d\xi_1 dt = d\mathbf{x}_1 d\xi_1 dt \int_{R^3} \int_{B^-} P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma\mathbf{n}, \xi_1, \xi_2, t) |\mathbf{V} \cdot \mathbf{n}| \sigma^2 d\mathbf{n} d\xi_2 \quad (1.2.5)$$

where  $B^-$  is the hemisphere corresponding to  $\mathbf{V} \cdot \mathbf{n} < 0$  (the particles are moving one toward the other before the collision). Thus we have the following result:

$$L = (N - 1)\sigma^2 \int_{R^3} \int_{B^-} P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma\mathbf{n}, \xi_1, \xi_2, t) |(\xi_2 - \xi_1) \cdot \mathbf{n}| d\xi_2 d\mathbf{n}. \quad (1.2.6)$$

The calculation of the gain term  $G$  is exactly the same as the one for  $L$ , except for the fact that we have to integrate over the hemisphere  $B^+$ , defined by  $\mathbf{V} \cdot \mathbf{n} > 0$  (the particles are moving away one from the other after the collision). Thus we have:

$$G = (N - 1)\sigma^2 \int_{R^3} \int_{B^+} P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma\mathbf{n}, \xi_1, \xi_2, t) |(\xi_2 - \xi_1) \cdot \mathbf{n}| d\xi_2 d\mathbf{n}. \quad (1.2.7)$$

We thus could write the right-hand side of Eq. (1.2.4) as a single expression:

$$G - L = (N - 1)\sigma^2 \int_{R^3} \int_{B} P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma\mathbf{n}, \xi_1, \xi_2, t) (\xi_2 - \xi_1) \cdot \mathbf{n} d\xi_2 d\mathbf{n} \quad (1.2.8)$$

where now  $B$  is the entire unit sphere and we have abolished the bars of absolute value in the right-hand side.

Eq. (1.2.8), although absolutely correct, is not so useful. It turns out that it is much more convenient to keep the gain and loss terms separated. Only in this way, in fact, can we insert in Eq. (1.2.4) the information that the probability density  $P^{(2)}$  is continuous at a collision; in other words, although the velocities of the particles undergo the discontinuous change described by Eqs. (1.2.1), we can write:

$$P^{(2)}(\mathbf{x}_1, \xi_1, \mathbf{x}_2, \xi_2, t) = P^{(2)}(\mathbf{x}_1, \xi_1 - \mathbf{n}(\mathbf{n} \cdot \mathbf{V}), \mathbf{x}_2, \xi_2 + \mathbf{n}(\mathbf{n} \cdot \mathbf{V}), t),$$

$$\text{if } |\mathbf{x}_1 - \mathbf{x}_2| = \sigma. \quad (1.2.9)$$

For brevity, we write (in agreement with Eq. (1.2.1):

$$\boldsymbol{\xi}'_1 = \boldsymbol{\xi}_1 - \mathbf{n}(\mathbf{n} \cdot \mathbf{V}) \quad \boldsymbol{\xi}'_2 = \boldsymbol{\xi}_2 + \mathbf{n}(\mathbf{n} \cdot \mathbf{V}). \quad (1.2.10)$$

Inserting Eq. (1.2.8) in Eq. (1.2.5) we thus obtain:

$$G = (N - 1)\sigma^2 \int_{R^3} \int_{\mathcal{B}^+} P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma\mathbf{n}, \boldsymbol{\xi}'_1, \boldsymbol{\xi}'_2, t) |(\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n}| d\boldsymbol{\xi}_2 d\mathbf{n} \quad (1.2.11)$$

which is a frequently used form. Sometimes  $\mathbf{n}$  is changed into  $-\mathbf{n}$  in order to have the same integration range as in  $L$ ; the only change (in addition to the change in the range) is in the second argument of  $P^{(2)}$ , which becomes  $\mathbf{x}_1 - \sigma\mathbf{n}$ .

At this point we are ready to understand Boltzmann's argument.  $N$  is a very large number and  $\sigma$  (expressed in common units, such as, e.g., centimeters) is very small; to fix the ideas, let us consider a box whose volume is  $1 \text{ cm}^3$  at room temperature and atmospheric pressure. Then  $N \cong 10^{20}$  and  $\sigma \cong 10^{-8} \text{ cm}$ . Then  $(N - 1)\sigma^2 \cong N\sigma^2 \cong 10^4 \text{ cm}^2 = 1 \text{ m}^2$  is a sizable quantity, while we can neglect the difference between  $\mathbf{x}_1$  and  $\mathbf{x}_1 + \sigma\mathbf{n}$ . This means that the equation to be written can be rigorously valid only in the so-called *Boltzmann-Grad limit*, when  $N \rightarrow \infty, \sigma \rightarrow 0$  with  $N\sigma^2$  finite.

In addition, the collisions between two preselected particles are rather rare events. Thus two spheres that happen to collide can be thought to be two randomly chosen particles and it makes sense to assume that the probability density of finding the first molecule at  $\mathbf{x}_1$  with velocity  $\boldsymbol{\xi}_1$  and the second at  $\mathbf{x}_2$  with velocity  $\boldsymbol{\xi}_2$  is the product of the probability density of finding the first molecule at  $\mathbf{x}_1$  with velocity  $\boldsymbol{\xi}_1$  times the probability density of finding the second molecule at  $\mathbf{x}_2$  with velocity  $\boldsymbol{\xi}_2$ . If we accept this we can write (assumption of *molecular chaos*):

$$P^{(2)}(\mathbf{x}_1, \boldsymbol{\xi}_1, \mathbf{x}_2, \boldsymbol{\xi}_2, t) = P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_1, t) P^{(1)}(\mathbf{x}_2, \boldsymbol{\xi}_2, t) \quad (1.2.12)$$

for two particles that are about to collide, or:

$$P^{(2)}(\mathbf{x}_1, \boldsymbol{\xi}_1, \mathbf{x}_1 + \sigma\mathbf{n}, \boldsymbol{\xi}_2, t) = P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_1, t) P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_2, t) \quad (1.2.13)$$

for  $(\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n} < 0$ .

Thus we can apply this *recipe* to the loss term (1.2.4) but not to the gain term in the form (1.2.5). It is possible, however, to apply Eq. (1.2.13) (with  $\boldsymbol{\xi}'_1, \boldsymbol{\xi}'_2$  in place of  $\boldsymbol{\xi}_1, \boldsymbol{\xi}_2$ ) to the form (1.2.9) of the gain term, because the transformation (1.2.10) maps the hemisphere  $\mathcal{B}^+$  onto the hemisphere  $\mathcal{B}^-$ .

If we accept all the simplifying assumptions made by Boltzmann, we obtain the following form for the gain and loss terms:

$$G = N\sigma^2 \int_{R^3} \int_{\mathcal{B}^-} P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}'_1, t) P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}'_2, t) |(\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n}| d\boldsymbol{\xi}_2 d\mathbf{n}, \quad (1.2.14)$$

$$L = N\sigma^2 \int_{R^3} \int_{\mathcal{B}^+} P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_1, t) P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_2, t) |(\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n}| d\boldsymbol{\xi}_2 d\mathbf{n}. \quad (1.2.15)$$

By inserting these expressions in Eq. (1.2.6) we can write the *Boltzmann equation* in the form

$$\begin{aligned} \frac{\partial P^{(1)}}{\partial t} + \boldsymbol{\xi}_1 \cdot \frac{\partial P^{(1)}}{\partial \mathbf{x}_1} = N\sigma^2 \int_{R^3} \int_{B^-} [P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}'_1, t)P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}'_2, t) \\ - P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_1, t)P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_2, t)] (\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n} |d\boldsymbol{\xi}_2 d\mathbf{n}. \end{aligned} \quad (1.2.16)$$

We remark that the expressions for  $\boldsymbol{\xi}'_1$  and  $\boldsymbol{\xi}'_2$  given in Eq. (1.2.1) are by no means the only possible ones. In fact we might use a different unit vector  $\boldsymbol{\omega}$ , directed as  $\mathbf{V}'$ , instead of  $\mathbf{n}$ . Then Eq. (1.2.1) is replaced by:

$$\begin{aligned} \boldsymbol{\xi}'_1 &= \bar{\boldsymbol{\xi}} + \frac{1}{2}|\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2|\boldsymbol{\omega}, \\ \boldsymbol{\xi}'_2 &= \bar{\boldsymbol{\xi}} - \frac{1}{2}|\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2|\boldsymbol{\omega} \end{aligned} \quad (1.2.17)$$

where  $\bar{\boldsymbol{\xi}} = \frac{1}{2}(\boldsymbol{\xi}_1 + \boldsymbol{\xi}_2)$  is the velocity of the center of mass. The relative velocity  $\mathbf{V}$  satisfies

$$\mathbf{V}' = \boldsymbol{\omega}|\mathbf{V}|. \quad (1.2.18)$$

The Boltzmann equation is an evolution equation for  $P^{(1)}$ , without any reference to  $P^{(2)}$ . This is its main advantage. However, it has been obtained at the price of several assumptions; the chaos assumption present in Eqs. (1.2.12) and (1.2.13) is particularly strong and requires to be discussed.

The molecular chaos assumption is clearly a property of randomness. Intuitively, one feels that collisions exert a randomizing influence, but it would be completely wrong to argue that the statistical independence described by Eq. (1.2.12) is a consequence of the dynamics. It is quite clear that we cannot expect every choice of the initial distribution of positions and velocities of the molecules to give a  $P^{(1)}$  which agrees with the solution of the Boltzmann equation in the Boltzmann–Grad limit. In other words molecular chaos must be present initially and we can only ask whether it is preserved by the time evolution of the system of hard spheres.

It is evident that the chaos property (1.2.12), if initially present, is almost immediately destroyed, if we insist that it should be valid everywhere. In fact, if it were strictly valid everywhere, the gain and loss terms, in the Boltzmann–Grad limit, would be exactly equal. As a consequence, there would be no effect of the collisions on the time evolution of  $P^{(1)}$ . The essential point is that we need the chaos property only for molecules which are about to collide, i.e., in the precise form stated in Eq. (1.2.13). It is clear then that even if  $P^{(1)}$  as predicted by the exact dynamics converges nicely to a solution of the Boltzmann equation,  $P^{(2)}$  may converge to a product, as stated in Eq. (1.2.11), only in a way which is in a certain sense very singular. In fact, it is not enough to show that the convergence is almost everywhere, because we need to use the chaos property in a zero measure set. On the other hand we cannot try to show that convergence holds everywhere,