

**3rd**  
EDITION

*Elements of*  
**Statistical  
Mechanics**

*D ter Haar*

# **ELEMENTS OF STATISTICAL MECHANICS**

TO MY WIFE

# ELEMENTS OF STATISTICAL MECHANICS

Third edition

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## TABLE OF CONTENTS

Preface to the third edition .....	ix
Preface to the second edition .....	xi
Preface to the first edition .....	xiii
 Chapter 1. The Maxwell distribution .....	 1
1.1. The Maxwell distribution .....	1
1.2. The perfect gas law .....	4
1.3. The van der Waals law .....	7
1.4. Collisions .....	11
1.5. The $H$ -theorem .....	19
1.6. The connection between $H$ and entropy .....	24
1.7. The connection between $H$ and probability .....	26
Problems .....	29
Bibliographical notes .....	32
 Chapter 2. The Maxwell-Boltzmann distribution .....	 36
2.1. The barometer formula .....	36
2.2. The $\mu$ -space .....	38
2.3. The $H$ -theorem; $H$ and probability .....	41
2.4. Applications of the Maxwell-Boltzmann formula .....	41
2.5. The Boltzmann transport equation .....	46
2.6. External parameters .....	48
2.7. The phase integral; connection with thermodynamics .....	49
Problems .....	52
Bibliographical notes .....	57
 Chapter 3. The partition function .....	 59
3.1. The partition function .....	59
3.2. The harmonic oscillator .....	61
3.3. Planck's radiation law .....	67
3.4. The transition to classical statistics .....	71
3.5. The rigid rotator: the hydrogen molecule .....	77
Problems .....	81
Bibliographical notes .....	85

## vi Contents

Chapter 4. Bose-Einstein and Fermi-Dirac statistics .....	88
4.1. Deviations from Boltzmann statistics .....	88
4.2. The probability aspect of statistics .....	90
4.3. The elementary method of statistics .....	97
4.4. Connection with thermodynamics .....	100
4.5. The Darwin-Fowler method .....	104
4.6. The perfect Boltzmann gas .....	111
4.7. The perfect Bose-Einstein gas .....	114
4.8. The perfect Fermi-Dirac gas .....	124
4.9. Are all particles bosons or fermions? .....	131
Problems .....	136
Bibliographical notes .....	144
Chapter 5. Classical ensembles .....	147
5.1. The $\Gamma$ -space; ensembles .....	147
5.2. Stationary ensembles .....	155
5.3. The macrocanonical ensemble .....	158
5.4. Fluctuations in a macrocanonical ensemble .....	162
5.5. The entropy in a macrocanonical ensemble .....	164
5.6. The coupling of two macrocanonical ensembles .....	169
5.7. Microcanonical ensembles .....	174
5.8. Application: the perfect gas .....	177
5.9. Grand ensembles .....	179
5.10. Fluctuations in a canonical grand ensemble .....	184
5.11. The coupling of two canonical grand ensembles .....	193
5.12. Application of the theory of classical grand ensembles to a perfect gas .....	196
5.13. The relationship between ensembles and actually observed systems .....	199
5.14. Ergodic theory and the $H$ -theorem in ensemble theory .....	204
Problems .....	210
Bibliographical notes .....	213
Chapter 6. The ensembles in quantum statistics .....	216
6.1. The density matrix .....	216
6.2. Pure case and mixed case .....	221
6.3. Macrocanonical ensembles in quantum statistics .....	224
6.4. Canonical grand ensembles in quantum statistics .....	227
6.5. The $H$ -theorem in quantum statistics .....	234
6.6. The perfect Boltzmann gas .....	239
6.7. The perfect Bose-Einstein gas .....	242
6.8. The perfect Fermi-Dirac gas .....	246
6.9. The Saha equilibrium .....	248
6.10. The relativistic electron gas .....	250
Problems .....	259
Bibliographical notes .....	265

Chapter 7. The equation of state of an imperfect gas .....	268
7.1. The equation of state .....	268
7.2. The van der Waals equation of state .....	274
Problems .....	284
Bibliographical notes .....	286
Chapter 8. The occupation number representation .....	288
8.1. Quasi-particles and elementary excitations .....	288
8.2. The occupation number representation for bosons .....	294
8.3. The occupation number representation for fermions .....	300
8.4. The Green function method in statistical mechanics .....	301
Problems .....	311
Bibliographical notes .....	313
Chapter 9. Phase transitions .....	315
9.1. Introduction .....	315
9.2. The liquid drop model of condensation .....	318
9.3. Mayer's theory of condensation .....	323
9.4. Yang and Lee's theory of phase transitions .....	328
9.5. The Ising model of ferromagnetism .....	335
9.6. The mean-field approximation .....	342
9.7. The quasi-chemical approximation .....	347
9.8. Critical phenomena .....	350
9.9. Some exact results .....	361
Problems .....	367
Bibliographical notes .....	370
Solutions to Selected Problems .....	375
Index .....	395





## PREFACE TO THE THIRD EDITION

It is nearly thirty years since the publication of the second edition and fully forty years after the publication of the first edition of this book. There have been many advances in statistical mechanics in that period, but it seems to me that the basic methods as described in the present book have been changed very little. This, combined with the urging of several friends and colleagues to make it again available, has persuaded me to present a third edition.

It will be seen that about two thirds of the book is essentially the same as it was in the first two editions. This refers especially to the first six chapters. The main change in those chapters since the second edition is that I have now included a discussion of the relation between spin and statistics in the main text and that I have mentioned anyons. My original intention was to devote more space to anyons and the rôle they play in the theory of the fractional quantum Hall effect and possibly in the theory of high-temperature superconductivity, but it soon became clear to me that in order to do this adequately I would have to go well beyond the general level of the book and also allot a disproportionate amount of space to the subject.

When I prepared the second edition it was my intention that it would be the first of a two-volume book, the second volume containing an update of those parts of the first edition which had not been covered in the first volume. This second volume was never written — to a large extent because developments had been so fast and extensive that I felt it was beyond my capability to do justice to the subject. However, this meant that such topics as the equation of state, phase transitions, the Ising model, and also modern ergodic theory, were not covered. This omission has now been made good to some extent in the present edition. Unfortunately the same reasons which made me omit a more extensive discussion of anyons also made me decide not to discuss in detail modern developments dealing with the foundations of statistical mechanics. However, I have once again a chapter on the equation of state, albeit not as extensive a one as in the first edition. Also, I have included again a chapter on phase transitions which follow to a large extent what was covered in the first edition, but with a more extensive discussion of Yang and Lee's theory of phase transitions — which appeared just when the manuscript for the first edition was completed — and a brief consideration of recent theories of critical phenomena, including

the renormalisation group method.

The only real new topic in this edition is covered in Chapter 8 where I discuss the occupation number representation and the Green function method. I had originally intended to cover also the statistical mechanics of solitons, but there again this would have made it necessary to include a thorough discussion of the inverse scattering technique and would lead to a disproportionate amount of space being devoted to a subject which, though extremely interesting, is not really central to modern statistical mechanics. I also had hoped to discuss diagram techniques, but when looking at them I found also here that this would involve expanding the book much more than I wanted to do and, moreover, I found that the variety of diagram techniques in statistical mechanics is *legio*: they range from the statistical mechanics counterpart of the quantummechanical Feynman technique to various *ad hoc* techniques — all demonstrating that diagram techniques are, indeed, essentially bookkeeping methods in perturbation theory.

Due partly to a desire not to make too many changes where I, possibly mistakenly, thought that the treatment was satisfactory and partly to the fact that in my retirement I do no longer have easy access to extensive library facilities the coverage of the literature since 1966 is far from satisfactory and I offer my sincere apologies for this — if I had tried to remedy this, I fear that this edition would never have been finished.

In conclusion I would like to thank many friends and colleagues for help in pointing out shortcomings and in helping me with references to more modern sources. I would especially like to mention Ian Aitchison, Dusan Radojicic, and Stig Stenholm.

D.t.H.

*Petworth, West Sussex*  
*February, 1994*

## PREFACE TO THE SECOND EDITION

More than thirteen years have elapsed since the manuscript of the first edition was completed. For some time it has been clear that a second edition was needed. In the last fifteen years statistical mechanics has developed at an enormous pace, and a textbook on statistical mechanics should take these developments into account. When I started to contemplate what changes should be made, it soon became clear that, if the book were to cover even approximately the same ground as the first edition did, it would have to be greatly expanded. It was then decided to split the book into two parts, the first volume covering the basic theory; a second volume, advanced theory. As a result, the present volume is now probably more suitable as a textbook for advanced undergraduate courses than the first edition was. To improve its usefulness a variety of problems has been included. I am greatly indebted to R.Kubo and the North-Holland Publishing Company for permission to incorporate some of the problems from Kubo's *Statistical Mechanics* and to the Oxford University Press for permission to incorporate problems from Oxford University Examination Papers. To some extent I have adopted Kubo's philosophy in that I feel that, to get the greatest advantage from the present volume, the student should work through most of the problems and so learn the subject by practising it. A number of topics—especially in the theory of metals and semiconductors—which were treated in the text of the first edition, have now been relegated to the problems section, partly to give the students experience in using statistical methods and partly to make room for other topics.

I should like to express my thanks to the many readers, users, and reviewers who have given me the benefit of their comments and criticism. In many cases I have followed their advice, and I have found that the reactions of my own students especially have been invaluable in finding out obscure passages that needed clarification.

I have finally had the strength of my convictions and have used Kramers' terminology "Thermostatistics" in the title of the second edition.

A comparison between the first edition and the second edition will show that the present volume contains Chapters I to IV of the first edition as Chapters 1 to 4; Chapters V and VI of the first edition make up the present Chapter 5, while Chapter VII becomes Chapter 6. Parts of Chapter IX of the first edition are incorporated in Chapter 4 and in a problem at

the end of Chapter 5; Chapters X and XI of the old edition have been nearly completely incorporated in various problems; and some topics of Chapter XIII have been put either in problems or in Chapters 5 and 6; Appendix II has become Chapter 8; Appendix III, Chapter 9; Appendix IV, Section 4.5; and Appendix VI, Chapter 7. The various parts of the mathematical appendix have been inserted at the appropriate spots in the earlier chapters. The main new topics covered in this book are the Saha equilibrium (Section 6.9), the Kramers-Casimir discussion of the third law (Section 9.2), fluctuations (Sections 7.1 and 7.2), and a more extensive discussion of the density matrix. A fair amount of new material is also to be found in the problems sections. Readers will probably also notice that the notation has been changed considerably to bring it in line with present-day practice.

Once again I appeal to readers and reviewers to let me have the benefit of their detailed criticism.

D.t.H.

*Magdalen College, Oxford*  
*May 1966*

## PREFACE TO THE FIRST EDITION

It is usual for an author to explain in a preface the reasons for writing the particular book which he is presenting to the public, to state who are the readers whom he has in mind for the book, to sketch the history of the writing of the book, and, last but not least, to express his thanks to all people who have been of assistance during the completion of the book.

The reason for writing another textbook on statistical mechanics was the feeling that there should be a textbook which combined in not too large a volume an outline of the main elements of statistical mechanics, starting from the Maxwell distribution and ending with quantum mechanical grand ensembles, with an account of a number of successful applications of these elements. Almost all existing textbooks stress only one or the other of these two aspects. It is hoped that readers will point out to me how far my own attempt has been successful, and I should at this point like to express the hope that reviewers will let me have the benefit of their detailed criticism.

The book is meant to be a textbook and is thus primarily intended for students. I have had in mind graduate students. This means that it should be used as a text for graduate lectures in the United States and for post-graduate lectures in the United Kingdom. It will probably be too advanced as a textbook for honours courses in British universities, although parts of it might be used as such and have been used as such by me. It is hoped that the book can also be used as a research tool and that it is possible to see from the applications how the theory might be applied to other subjects. For that reason I have tried to give as complete a bibliography as was feasible in the framework of a textbook. As the manuscript of the book was essentially completed at the beginning of 1952, references to papers published in 1951 or 1952 will not be complete.

A first rough outline of the book was sketched during the last war-winter in Leiden. A number of students were deprived of the regular courses because Leiden University was closed by the occupying authorities, and the outline of the present book served as a substitute for the regular statistical mechanics course. The manuscript then rested until I wrote the first draft of Parts A and B at Purdue University during 1947-1948. There was another interval until 1950, when I came to St. Andrews, where the manuscript in its present form was started and finished.

It is a pleasant task to thank the many physicists who have given me their advice on parts of the manuscript. My thanks are particularly due

to Professors F.J.Belinfante, H.M.James, K.Lark-Horovitz, H.Margenau, R.E.Peierls, and F.E.Simon, who have helped me with their criticism and advice. If the approach is sometimes not very clear and if my English has sometimes a distinct foreign flavour, it cannot be blamed on Professor F.Y.Poynton, who has tried to make Parts A and B as far as possible easy reading for students, or on Professors E.S.Akeley and J.F.Allen, who have tried to weed out of the text all barbarisms. I should like to express to them my warmest gratitude. Finally I should like to express my great indebtedness to Professor H.A.Kramers. Anybody who is familiar with his lectures on statistical mechanics will immediately see how much this book owes to him. It is far from a platitude to say that it would never have been written but for Professor Kramers. Not only did he give me an outline of the contents of Parts A and B; in discussions and lectures he has taught me the fundamental ideas of the subject. I can therefore with some justification claim that the method of treatment in Parts A and B goes straight back to Boltzmann, via Kramers and Ehrenfest. Large parts of the book are, indeed, nearly wholly based on a series of lectures given by Professor Kramers in Leiden during 1944-1945.

In conclusion, I should like to express my thanks to Professor K.Lark-Horovitz and Miss A.Scudder for their help in editing the manuscript.

D.t.H.

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*January, 1954*

## CHAPTER 1

# THE MAXWELL DISTRIBUTION

### 1.1. The Maxwell Distribution

Equilibrium statistical mechanics, or "thermostatistics", to use a term coined by Kramers,<sup>1</sup> is that branch of physics which attempts to derive the equilibrium or thermal properties of matter in bulk, and of radiation, from the properties of the constituent particles. Such an atomistic interpretation of the thermal properties of matter was first attempted in the kinetic theory of gases, developed in the nineteenth century by Clausius, Maxwell, and Boltzmann. In this theory it was shown how such phenomenological concepts as temperature and entropy could be interpreted in terms of the *average* properties of the particles that were the constituent parts of the system under consideration. Kinetic theory could be applied as long as one could either completely neglect the interactions between the particles or could neglect them to a first approximation, taking them into account in a second approximation. Such an approach leads, for instance, to the van der Waals law of an imperfect gas, as we shall see in § 1.3 of this chapter. In most physical systems, however, this approach is much too simplified, and one needs have recourse to more sophisticated methods of averaging.

This more sophisticated approach is statistical mechanics proper, a term coined by J.W. Gibbs in 1901 for that branch of rational mechanics which deals statistically with systems consisting of large numbers of constituents. In the first four chapters we shall consider systems of independent particles, a subject which is really part of kinetic theory, while in later chapters we shall consider statistical mechanics proper. The reason for using statistical methods to treat physical systems is partly because they are so complicated that they present us with "well-nigh unsurmountable mathematical difficulties",<sup>2</sup> if we try to solve their equations of motion exactly; and partly because, even if we could solve these equations of motion exactly, we have only incomplete experimental data from which we can obtain the boundary conditions for the equations of motion.

In the present chapter we shall confine ourselves to the simplest possible

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<sup>1</sup> H.A. Kramers, *Nuovo cimento* 6 Suppl., 158 (1949).

<sup>2</sup> H.A. Kramers, *ibid.*



## 2 The Maxwell Distribution

system: a monatomic gas, that is, a system of point particles, enclosed in a vessel of volume  $V$  without any external forces acting upon the gas apart from the forces which the walls of the vessel will exert upon the gas and which, in fact, will keep the gas within the vessel. We introduce Cartesian coordinates  $x$ ,  $y$ , and  $z$  to describe the system; the position of the  $i$ -th particle is thus determined by its three position coordinates  $x_i$ ,  $y_i$ , and  $z_i$ , or by the vector  $\mathbf{r}_i$ .<sup>3</sup> We denote by  $u$ ,  $v$ , and  $w$  the  $x$ ,  $y$ , and  $z$  components of a velocity  $\mathbf{c}$ , and  $u_i$ ,  $v_i$ , and  $w_i$  are thus the components of the velocity  $\mathbf{c}_i$  of the  $i$ -th particle. Once the positions and velocities of all the atoms are given, the microscopic behaviour of the system is completely determined, provided the interatomic forces and the forces exerted by the walls on the atoms are known. If  $N$  is the number of atoms in the system, we need  $6N$  quantities, for instance,  $x_i$ ,  $y_i$ ,  $z_i$ ,  $u_i$ ,  $v_i$ ,  $w_i$  ( $i = 1$  to  $N$ ) to determine the microscopic behaviour. However, usually we are interested in only a few combinations of these  $6N$  quantities which will determine the macroscopic behaviour of the system. We mentioned a moment ago that the exact knowledge of all  $6N$  coordinates and velocities is outside the experimental possibilities, while the computation of their values from the equations of motion is outside our mathematical powers, as  $N$  is usually an extremely large number — of the order of  $10^{25}$  for one  $\text{m}^3$  of a gas at NTP. We can use that fact that  $N$  is such a huge number to apply statistical methods in the safe knowledge that, because of the extremely large numbers of degrees of freedom, fluctuations will in general be small (compare §§ 5.4 and 5.10).

Let us for the moment neglect first of all the influence of the wall and secondly possible fluctuations. In that case the number of atoms in a unit volume of the gas will be independent of the position of that unit volume in the gas. If we denote the number of atoms per unit volume by  $n$ , we have

$$n = \frac{N}{V}. \quad (1.101)$$

Let us denote by

$$f(u, v, w) du dv dw$$

the number of atoms per unit volume, the velocity components of which lie in the specified intervals  $(u, u + du)$ ,  $(v, v + dv)$ , and  $(w, w + dw)$ . The function  $f(u, v, w)$  will be called the *distribution function*. It determines the fraction of atoms with velocities within given intervals. This fraction is obtained by dividing  $f(u, v, w)$  by  $n$ .

We shall call the Cartesian three-dimensional space in which we can plot the  $x$ ,  $y$ , and  $z$  components of the velocities *velocity space*, and the point  $u, v, w$  in velocity space will be called the *representative point* of an atom with velocity components  $u$ ,  $v$ , and  $w$ .

From the definition of  $f(u, v, w)$  it follows that it satisfies a *normalisation*

---

<sup>3</sup> Vectors are denoted by bold face italic type.

condition:

$$\int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dw f(u, v, w) = n. \quad (1.102)$$

In the present chapter we shall assume that  $f(u, v, w)$  is not only independent of  $x$ ,  $y$ , and  $z$ , but also does not depend explicitly upon the time  $t$ . Let  $A$  be a quantity that is a function of the velocity components of an atom, but which does not depend explicitly on either  $x$ ,  $y$ , and  $z$  or  $t$ . As an example we may give the kinetic energy of an atom. We can now ask for the *average value*,  $\bar{A}$ , of  $A(u, v, w)$ , where the average is taken over all atoms of the gas and where the average value is equivalent to the arithmetic mean, that is, defined by the equation

$$\bar{A} = \frac{1}{n} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} du dv dw A(u, v, w) f(u, v, w). \quad (1.103)$$

Neither  $A$  nor  $f$  depends on  $x$ ,  $y$ ,  $z$ , or  $t$  so that  $\bar{A}$  will also be independent of  $x$ ,  $y$ ,  $z$ , and  $t$ .

In the following sections of this chapter it will be proved that the distribution function of a gas in equilibrium at an absolute temperature  $T$  will be given by the equation

$$f(u, v, w) = n \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-m(u^2+v^2+w^2)/2kT}, \quad (1.104)$$

where  $m$  is the mass of one atom and  $k$  Boltzmann's constant.<sup>4</sup> The distribution given by Eq.(1.104) is called the *Maxwell distribution* and was first introduced by Maxwell in 1859. It can easily be shown that the  $f(u, v, w)$  given by Eq.(1.104) satisfies Eq.(1.102). Equations (1.103) and (1.104) can now be used to calculate average values.

Denoting by  $c$  the absolute value of the velocity of an atom,

$$c^2 = u^2 + v^2 + w^2, \quad (1.105)$$

and by  $\mathcal{T}(= \frac{1}{2}mc^2)$  the kinetic energy of an atom, we have

$$\overline{c^2} = \frac{3kT}{m}, \quad (1.106)$$

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}}, \quad (1.107)$$

$$\bar{u} = \bar{v} = \bar{w} = 0, \quad (1.108)$$

$$\overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{kT}{m}, \quad (1.109)$$

$$\bar{\mathcal{T}} = \overline{\frac{1}{2}mc^2} = \frac{3}{2}kT. \quad (1.110)$$

<sup>4</sup> Boltzmann never deduced the value of  $k$ ; this was first done by Planck in 1900 in connection with his radiation law. Smekal (*Enzyklopädie der Mathematischen Wissenschaften*, Vol.V, Part 28, Leipzig-Berlin, 1926) and Meissner (*Science*, 113, 78, 1951) suggest calling  $k$  the Boltzmann-Planck constant. It is interesting to note that Lorentz (see, for example, *Lectures in Theoretical Physics*, Vol.II, p.175, London 1927) calls  $k$  Planck's constant!

## 4 The Maxwell Distribution

There are three points in connection with Eqs.(1.106) to (1.110) worth noting:

1. Compare Eqs.(1.106) and (1.107). We see that there exists a difference between the mean absolute velocity  $\bar{c}$  and the root-mean-square velocity  $\sqrt{c^2}$ :

$$\sqrt{c^2} = \sqrt{\frac{3\pi}{8}} \bar{c} = 1.085 \bar{c}. \quad (1.111)$$

2. Equation (1.110) shows that the mean kinetic energy is independent of the mass of the atoms. Thus we get the same result for any gas, provided the temperature is the same. We can therefore use Eq.(1.110) as a definition of the temperature of a gas.
3. From Eq.(1.109) it follows that the average kinetic energy pertaining to the  $x$ ,  $y$ , or  $z$  direction is the same and is equal to one third of the average total kinetic energy. This is an example of the *equipartition of kinetic energy*.

### 1.2. The Perfect Gas Law

In this section we shall assume that there is no interaction between the atoms of the gas which we are considering.

If we assume that the distribution function is given by Eq.(1.104), we can calculate the pressure of the gas in terms of  $n$  and  $T$ . Two derivations of the formula for the pressure will be given. The first derivation is due to Clausius and the second one to Lorentz.

In order to derive the formula in the way it was done by Clausius, we must remember that according to Newton's second law force is equivalent to the rate of change of momentum. The pressure of the gas is defined either as the force exerted by the gas on unit area of the wall, or as the total transfer of momentum per unit time from the gas to unit area of the wall. The Cartesian axes will be chosen in such a way that the negative  $x$  axis falls along the normal to the wall (see Fig.1.1). We shall again neglect any effect arising from a possible potential energy between the wall and the gas atoms, and we shall assume that the atoms will be perfectly reflected by the wall.

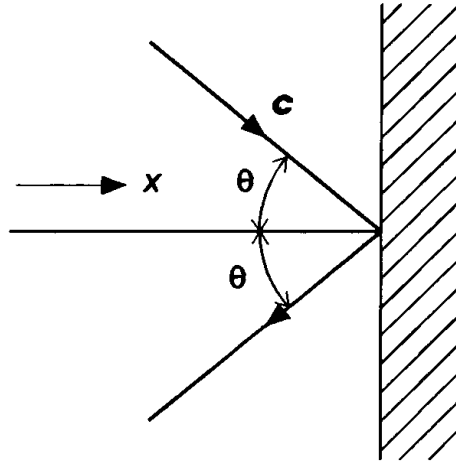
In the case of a perfect reflection, only the velocity component perpendicular to the wall will change during the collision of a gas atom with the wall. This component will change its sign, but the other components will remain unchanged. If an atom with velocity  $c$  strikes the wall at an angle  $\theta$  to the normal, the momentum transferred during the collision will be given by the expression

$$2mc \cos \theta = 2mu. \quad (1.201)$$

In order to calculate the total transfer of momentum, we must next determine the number of collisions per unit time per unit area. For a given velocity  $c$  this number is zero, if  $u$  is negative. If  $u$  is positive, the number of collisions is given by the total number of atoms contained in a cylinder

with a base of unit area and a slant height  $c$ , parallel to  $\mathbf{c}$ . The volume of this cylinder is  $c \cos \theta$ . If the number of atoms per unit volume with given velocity  $\mathbf{c}$  is  $n(\mathbf{c})$ , the number of collisions  $N_{\text{coll}}$  per unit time per unit area will be given by the equation

$$N_{\text{coll}}(\mathbf{c}) = n(\mathbf{c}) c \cos \theta = n(\mathbf{c}) u. \quad (1.202)$$



**Fig.1.1.** The elastic reflection of a point particle by a wall. The normal to the wall is along the negative  $x$ -axis, and a particle with velocity  $\mathbf{c}$  strikes the wall at an angle  $\theta$  to the normal.

The total momentum transferred to unit area of the wall per unit time by atoms of a given velocity  $\mathbf{c}$  is found by combining Eqs.(1.201) and (1.202) and is equal to

$$2m n(\mathbf{c}) u^2. \quad (1.203)$$

The function  $n(\mathbf{c})$  will be the distribution function  $f(u, v, w)$ , which is assumed to be given by Eq.(1.104). To obtain the pressure  $P$  we must integrate expression (1.203) over all velocities for which  $u \geq 0$ , so that we get

$$P = 2m \int_0^{+\infty} du \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dw f(u, v, w) u^2,$$

or,

$$P = nkT. \quad (1.204)$$

Equation (1.204) is called the *perfect gas law* or the Boyle–Gay-Lussac law.

Introducing the absolute gas constant  $R$  by the equation

$$R = kN_A, \quad (1.205)$$