

# Chapter 1

## Introduction to Part I

### 1.1 Aim of these lecture notes

Ludwig Boltzmann is known to physicists for a number of important results in statistical mechanics, as indicated below:

#### Ludwig Boltzmann (1844-1906)



*H-theorem*

$$S = k \ln \Omega$$

*Second law of Thermodynamics*

"I know much better how to integrate than to intrigue."

In 1872 he presented his eponymous kinetic equation for the *velocity distribution function* of a gas, which completely describes its physical properties. (See, e.g., the special volume dedicated to this work a century later, by E.G.D. Cohen and W. Thirring, "The Boltzmann equation and applications" (Springer, 1973)) The present lectures focus on the basic ideas of kinetic theory emanating from that time to the present, as applied to the calculation of transport properties

of dilute charged particles in gases subject to strong external fields. It is emphasized that the systems considered are generally far from equilibrium, and it is no use simply "assuming a Maxwellian distribution function". Indeed, in any serious study of matter in bulk, one must *calculate* the velocity distribution function for the problem at hand, *not assume it*. The aim of this course is to equip students with the means to be able to do just this, and especially to understand:

- The basic ideas of kinetic theory and kinetic equations in particular
- How microscopic collision dynamics are reflected in macroscopic transport properties
- The basic techniques for calculating transport coefficients

*Straightforward mathematics and short physical arguments take precedence over rigorous analysis.*

## 1.2 Reading material for Part I

- A good introductory background to kinetic theory can be found in the following article:

E.D.G. Cohen, Amer. J. Phys. 61, 524 (Sections I and II A,B,C only)

- It is suggested that students with a sound background in statistical mechanics read these lectures in conjunction with:

*K. Huang, "Statistical mechanics" 2<sup>nd</sup> Edition (Wiley, 1987), especially Chapters 3-5*

- Introductory texts on statistical and classical mechanics respectively include:

*D. V. Schroeder, "Thermal physics" (Addison-Wesley, Longman, 2000), and*

*H. Goldstein, "Classical mechanics", 2<sup>nd</sup> Edition (Addison-Wesley, 1980)*

- As regards the kinetic theory of charged particles in gases specifically, students may find the following older texts user-friendly:

*M.A. Uman, "Introduction to plasma physics" (McGraw-Hill, 1964)*  
*D.C. Montgomery and D.A. Tidman, "Plasma kinetic theory", (McGraw-Hill, 1964)*  
*E.H. Holt and R.E. Haskell, "Plasma dynamics" (Macmillan, 1965)*

- Research-level books referred to in these lectures:

*L. G. H. Huxley and R. W. Crompton, "The Diffusion and Drift of Electrons in Gases" (Wiley, 1974)*  
*E. W. McDaniel and E. A. Mason, "The Mobility and Diffusion of Ions in Gases" (Wiley, 1973)*  
*E. A. Mason and E. W. McDaniel, "The Transport Properties of Ions in Gases" (Wiley, 1988)*

- Advanced general kinetic theory references:

*R.L. Liboff, "Kinetic theory" , 2<sup>nd</sup> edition (Wiley, 1998), Chs. 3 & 4*  
*A.R. Hochstim and G. Massell, "Kinetic processes in gases and plasmas" (Academic Press, 1969)*  
*S. Chapman and T.G. Cowling, "The mathematical theory of non-uniform gases", 3<sup>rd</sup> edition (Cambridge, 1970)*

- References to journal articles will be given as we go along. See also the bibliography in the next section.

### 1.3 Brief literature survey

Studies of charged particles in gases go back many years to the birth of modern atomic physics late in the nineteenth and early in the twentieth centuries respectively. Experiments by J.J. Thomson, Townsend and others helped prove the existence of electrons and ions, while the famous Franck-Hertz experiment confirmed Bohr's postulates on the quantization of atomic energy states. Huxley and Crompton [1], Loeb [2], McDaniel and Mason [3] and Mason and

McDaniel [4] give comprehensive reviews of this early work. Nowadays drift tube experiments provide accurate information about fundamental ion and electron scattering cross sections at low energy ( $\lesssim 1eV$ ) for which there is a high demand in diverse scientific areas such as astrophysics, gas lasers, high energy particle accelerator detectors, to name but a few. Moreover, there has been a huge worldwide investment of resources in technologies associated with charged particles in gases, in the microchip industry in particular, for which the annual contribution to the world economy amounts to many billions of dollars [5]. Given the ever decreasing size of microchips, and the corresponding need for greater precision, the full potential of this technology can be realised only when the basic physics has been mastered [6].

At the heart of our study is the 1872 Boltzmann kinetic equation [7,8], which has been reviewed extensively and frequently in the context of charged particle transport. Lucid reviews by Wannier [9] and Allis [10] in the 1950's were followed by the seminal papers of Kumar [11], who introduced the techniques of atomic and quantum physics into kinetic theory, and by Mason, Viehland and collaborators [5], who developed solutions of Boltzmann's equation in strong field, highly nonequilibrium situations. After comprehensive reviews in the early 1980's by Kumar and collaborators [12, 13], the modern era of kinetic theory was well and truly underway. More recently, Crompton followed up his earlier book [1] by summarizing drift tube experiments and their application to determination of electron-molecule cross sections in some detail [14]. The current state of affairs in charged particle transport theory can be ascertained from refs [15] and [16]. Nowadays transport theory works in tandem with both multiple-scattering drift tube and single-scattering beam experiments [17] to provide a comprehensive picture gaseous charged particle phenomena at both the microscopic and macroscopic levels.

It has long been known that there is a one-to-one correspondence between charged carriers in gases and semiconductors, involving collisions with gas atoms and molecules on the one hand, and phonons on the other. This is particularly interesting in the context of soft condensed matter, which exhibits many unusual properties [18]. There is also a less well known application to turbulent dispersion of a

“passive additive” in the turbulent atmospheric boundary layer, but that is another story. Let us just say that many of the techniques of kinetic theory carry over to other areas of physics, and that these lectures should be viewed in that broader context.

### References

- [1] L. G. H. Huxley and R. W. Crompton, "The Diffusion and Drift of Electrons in Gases" (Wiley, 1974)
- [2] L.B. Loeb, "Basic Processes of Gaseous Electronics" (University of California Press, 1955)
- [3] E. W. McDaniel and E. A. Mason, "The Mobility and Diffusion of Ions in Gases" (Wiley, 1973)
- [4] E. A. Mason and E. W. McDaniel, "The Transport Properties of Ions in Gases" (Wiley, 1988)
- [5] K. Becker, H. Deutsch, and M. Inokuti, *Adv. At. Mol. Opt. Phys.* 43, 399 (2000)
- [6] M.A. Liebermann and A.J. Lichtenberg, "Principles of plasma discharges and materials processing" (Wiley, 1994); T. Makabe, "Advances in low temperature r.f. plasmas" (Elsevier, 2002)
- [7] L. Boltzmann, *Wien. Bericht* 66, 275 (1872)
- [8] E.G.D. Cohen and W. Thirring, "The Boltzmann equation and applications" (Springer, 1973)
- [9] G.H. Wannier, *Bell Syst. Tech. J.* 32, 170 (1953)
- [10] W.P. Allis, in *Handbuch der Physik*, Vol 21, p. 383 (Springer, 1956)
- [11] K. Kumar, *Aust. J. Phys.* 20, 205 (1967)
- [12] K. Kumar et al, *Aust. J. Phys.* 33, 343 (1980)
- [13] K. Kumar, *Phys. Rep.* (1984) 112, 319 (1984)
- [14] R.W. Crompton, *Adv. At. Mol. Opt. Phys.* 32, 97 (1994)
- [15] R.D. White et al, *Appl. Surface Sci.* 192, 26 (2002); L.A. Viehland, *Phys. Scripta T53*, 53 (1994)
- [16] R.E. Robson et al, *Rev. Mod. Phys.* (in press, 2005)
- [17] M.A. Brunger and S.J. Buckman, *Phys. Rep.* 357, 212 (2002)
- [18] I.M. Sokolov et al, "Fractional kinetics", *Phys. Today*, Nov., 2002; R.E. Robson and A. Blumen, *Phys. Rev. E* 71, 061104 (2005)

## 1.4 Experiment and theory

Statistical mechanics provides the link between microscopic and macroscopic descriptions of matter, and kinetic theory is that branch of statistical mechanics which describes systems through a *velocity distribution function*  $f(\mathbf{v})$ . The main application of the kinetic theory formulation described in these lectures has been to *drift tube experiments*, where ions or electrons undergo a large number of *collisions* with the target atoms and/or molecules of a gas in a drift chamber, as they move from the source to the collecting electrode. Such arrangements are to be distinguished from *single-scattering beam experiments*, in which a highly focussed, energetically-resolved beam of particles is incident with given velocity  $\mathbf{v}_I$  on a confined region of gas: in that type of experiment, effectively  $f(\mathbf{v}) \sim \delta(\mathbf{v} - \mathbf{v}_I)$  is prescribed. In contrast, for a drift tube experiment, one has control over only few *macroscopic* variables (e.g., gas temperature and density, field strength) and analysis of this (or indeed any macroscopic system) requires *calculation of  $f(\mathbf{v})$*  from a kinetic equation, in the manner described in these lectures. The distinction between the two types of experiment is clear enough, but there are plenty of misunderstandings in the literature, even in standard text books. For example, the famous Franck-Hertz experiment, which helped establish the quantum foundations of modern atomic physics, is in fact a type of multiple-scattering drift tube experiment, although it is often mistakenly discussed in single scattering terms.

The application of kinetic theory to drift tube experiments is shown schematically in Fig. 1.1. As indicated, other kinetic equations have been developed since Boltzmann's original work. Our task is to solve the appropriate kinetic equation and find  $f(\mathbf{v})$ , or of more direct relevance to experiment, its velocity "moments". Fig. 1.2 illustrates the general drift tube experiment, while Fig.1.3 illustrates a travelling pulse in the canonical *time-of-flight experiment*.

One of the most important applications of the transport theory discussed in these lectures has been to unfold drift tube experimental data to obtain cross sections and/or interaction potentials. As shown in Fig.1.4 this amounts to an iteration process in which one

What is measured in a drift tube experiment?

"Moments" of the charged particle velocity distribution function, e.g.,

- Number density  $n = \int f(\mathbf{v}) d\mathbf{v}$

- Average velocity  $\langle \mathbf{v} \rangle = \int \mathbf{v} f(\mathbf{v}) d\mathbf{v} / \int f(\mathbf{v}) d\mathbf{v}$

How is  $f(\mathbf{v})$  found?

From a kinetic equation (equation of continuity in phase space)

- Boltzmann equation 1872 (elastic collisions)
- Wang-Chang, Uhlenbeck, de Boer 1951 (semi-classical inelastics)
- Waldmann-Snyder 1958 - 61 (quantum effects, density matrix)

Figure 1.1: Schematic outline of the way in which kinetic theory is applied to drift tube experiments.

starts with a set of trial cross sections, and compares transport coefficients derived from solving Boltzmann's kinetic equation with those measured in experiment, followed by further refinement of the cross sections and so on, until there is agreement to within some prescribed accuracy. Note that at low energies, say  $\epsilon \lesssim 0.5$ , where so much interesting atomic and molecular physics occurs, these accuracies are still generally better than can be achieved with modern day beam experiments. However, nowadays, the *same* kinetic theory now finds increasing application in low temperature plasma technology, as indicated in Fig. 1.5, in which the cross sections are *input*, e.g., from *ab initio* quantum mechanical calculations, drift tube and/or beam experiments.

As already remarked, there are many other diverse areas of application, such as high energy particle detectors, ionospheric physics, gas lasers, cold fusion, spectral line broadening, to name just a few

Swarm experiment (energies  $> 1/40$  eV) (R.W. Crompton, 1994)

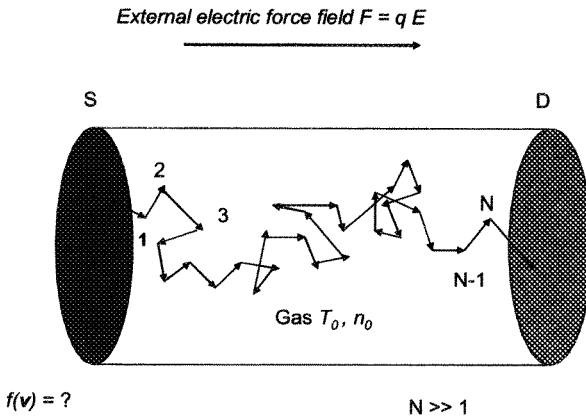


Figure 1.2: Schematic illustration of a drift tube experiment, in which a few macroscopic properties, such as field strength and gas temperature are controlled, but the detailed multi-scattering events are not. This experiment relies upon kinetic theory to furnish the velocity distribution function  $f(\mathbf{v})$ , from which fundamental scattering cross sections may be unfolded from the measured transport coefficient data.

areas, such is the generality of the theory, and the relative ease with which theoretical physicists may skip between fields. In some areas it is fair to say that theory leads experiment. The curious phenomenon of negative absolute mobility (current flowing the wrong way) of electrons in strongly attaching gases is an example of that: it has been predicted theoretically in a number of independent theoretical studies, but has never been observed in experiment as explained in *J. Chem. Phys.* 119, 11249 (2003) .

This is where these lectures take us eventually, but for now we start right at the beginning.

## Time of flight experiment

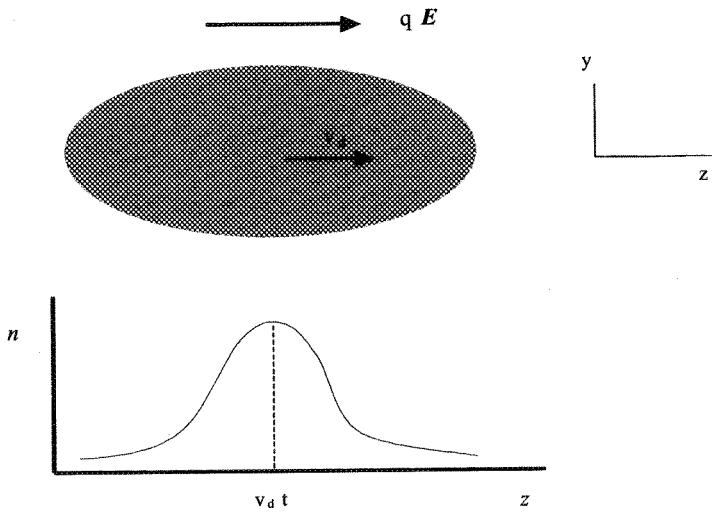


Figure 1.3: The time-of-flight experiment is common to both gaseous and condensed matter physics. Transport coefficients are determined by measuring the time it takes for a pulse of charge carriers to drift a known distance in a known time.

### Traditional drift tube program

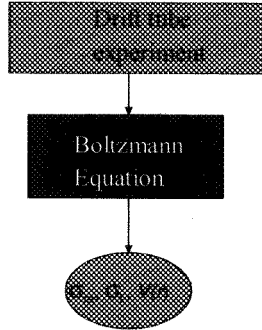


Figure 1.4: One of the main uses of charged particle transport theory has traditionally been to unfold the scattering cross sections  $\sigma_m$ ,  $\sigma_I$  and/or interaction potentials  $V(r)$  embedded in transport coefficient data measured in drift tube experiments

### Present day theoretical program

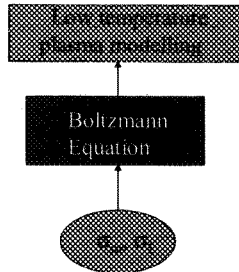


Figure 1.5: Nowadays cross sections are more commonly taken as given, eg, from single particle beam experiments or theoretical calculations, and used to produce macroscopic quantities of interest, notably in modelling of low-temperature plasmas.