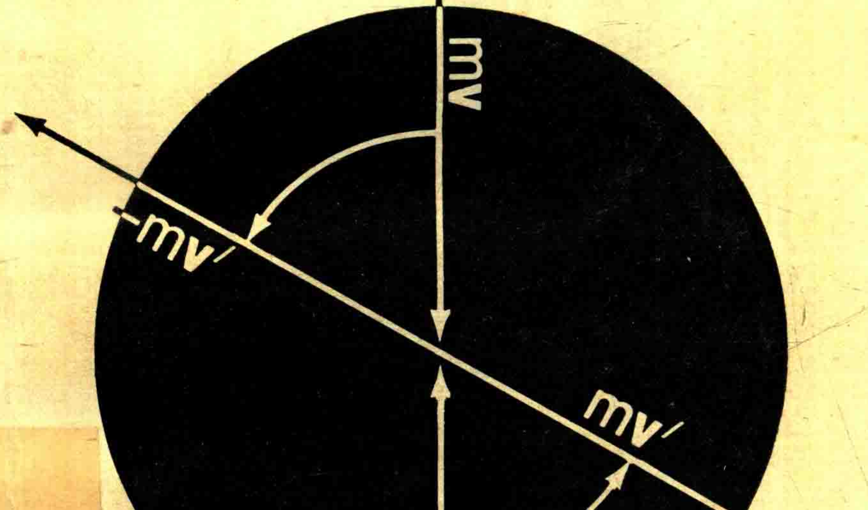
introduction to

# atomic and molecular collisions



R. E. JOHNSON

# Introduction to
# ATOMIC AND MOLECULAR COLLISIONS

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# Preface

In working with graduate students in engineering physics at the University of Virginia on research problems in gas kinetics, radiation biology, ion–materials interactions, and upper-atmosphere chemistry, it became quite apparent that there was no satisfactory text available to these students on atomic and molecular collisions. For graduate students in physics and quantum chemistry and researchers in atomic and molecular interactions there are a large number of excellent advanced texts. However, for students in applied science, who require some knowledge and understanding of collision phenomena, such texts are of little use. These students often have some background in modern physics and/or chemistry but lack graduate-level course work in quantum mechanics. Such students, however, tend to have a good intuitive grasp of classical mechanics and have been exposed to wave phenomena in some form (e.g., electricity and magnetism, acoustics, etc.). Further, their requirements in using collision processes and employing models do not generally include the use of formal scattering theory, a large fraction of the content of many advanced texts. In fact, most researchers who work in the area of atomic and molecular collisions tend to pride themselves on their ability to describe results using simple theoretical models based on classical and semiclassical methods.

This book was written in order to allow a student to develop an understanding of atomic and molecular collision phenomena based on those classical and semiclassical methods and approximations employed frequently in the literature. The book is aimed at the scientist or engineer in such fields as engineering physics, materials science, chemistry, astronomy, aerospace engineering, nuclear engineering, electrical engineering, radiation biology, atmospheric and solar physics, and plasma science, and who requires an understanding of atomic and molecular interactions and collisions to better understand, for example, chemical kinetics, gas dynamics, laser processes, interactions of radiation with materials, etc. However, the book should also be useful to physics and quantum chemistry students actually working on atomic collisions and molecular interaction problems. Having been such a student myself, I found it took a remarkable amount of time to develop the intuitive grasp that was used by workers already in the field in discussing collision-related problems. It was even more difficult to obtain a clear view of the usefulness of the measurements and calculations produced. Therefore, in this book some time is spent discussing, first qualitatively and later in a simple quantitiative way, applications of cross section and reaction rate results to a few macroscopic phenomena controlled by molecular-level events. The problem areas chosen for consideration are ones of which I had at least peripheral knowledge, and I apologize in advance for not including particularly obvious areas dear to some readers' hearts. However, a final purpose of this book is to make clear the commonality of methods and approximations used in dealing with effects controlled by electrons, ions, atoms, and molecules.

This book is written as a graduate-level text for a one-semester course and includes problems and a general bibliography at the end of each chapter. However, it is also hoped that, with the material presented in the appendixes, this book will be a useful reference for classical and semiclassical formulas that are often employed in the literature. Some of the problems and the appendixes are, simply, derivations of results presented in order to keep the text short and, hopefully, keep the interest and involvement of the reader high. In the first chapter, a rationale and a perspective are given for understanding the collisions of atoms and molecules. A number of collision-related macroscopic phenomena are discussed qualitatively with the role of atomic and molecular interactions delineated. In this chapter the type of information required regarding collisions is determined. In the second chapter, the notion of a cross section is developed and then related to collision quantities discussed above. This is followed by a classical treatment of collisions. The pace in this chapter is slow at first, with words used where in many texts mathematical expressions would suffice. However, I felt that if the definition of a cross section was quite clear at the outset even readers unfamiliar with collision concepts could follow the subsequent, much more terse presentations. In the rest of the text I continuously relate back to the ideas developed in Chapter 2.

Background material on wave mechanics and atomic and molecular notation are given in Chapter 3 in order that students who have had only basic instruction in this area can easily follow the discussion of the wave mechanical description of collisions. The description of molecular interactions is completed in Chapter 4, where interaction potentials (which are required to determine the motion of the colliding particles) and transition probabilities (which describe inelastic effects) are calculated. Students specializing in collision research, having a strong background in quantum mechanics, should be able to read this portion of the text and work out the problems on their own in a short period of time as, for instance, preparation for starting dissertation work. The latter part of Chapter 4, on the other hand, may prove to be rather terse for readers unfamiliar with the methods of modern physics. However, I feel the support material is available in earlier chapters and in the appendix, and this material, with patience, is understandable and clearly worthwhile. Up to this point in the presentation, little in the way of experimental data is presented since such results cannot be described clearly without an understanding of both the calculation of the cross sections and the nature of the potentials and transition probabilities. Therefore, in Chapter 5, I present a summary of experimental results for cross sections and rate constants and relate these to the cross-section models and potentials discussed earlier. This is followed, in Chapter 6, by a return to the material presented in Chapter 1. Now, however, estimates of the collision quantities are made in order to describe, in a simple, quantitative way, certain phenomena determined by molecular collisions.

In writing this book I would first like to acknowledge the benefit of a sabbatical leave of absence from the University of Virginia spent at Harvard University. I would also like to thank R. G. Cooks (Purdue University) and M. Inokuti (Argonne National Laboratory) for a careful reading of the manuscript and many helpful comments and criticisms. The following students, who read a draft of the manuscript as part of a course in engineering physics, were also very helpful: G. Cooper, R. Evatt, P. Wantuck, and E. Sieveka. A number of colleagues also read and criticized various sections of the book: J. R. Scott and J. W. Boring (University of Virginia), T. A. Green (Sandia Corporation), G. Victor and W. A. Traub (Harvard-Smithsonian Astrophysical Observatory), W. L. Brown (Bell Laboratory), S. Hamasaki (Jaycor Corporation), J. B. Delos (College of William and Mary), R. B. Bernstein (Columbia University), P. Sigmund (Odense University), and U. Fano (University of Chicago). Finally, I would like to thank my father, T. J. Johnson, for producing many of the illustrations used and my family for their support and encouragement while writing this text.

R. E. Johnson

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# 1

# Application Areas

## Introduction

The need to understand the behavior of colliding atoms and molecules is self-evident as we live in a world constructed from atomic building blocks. This is not a static construction of the type envisaged early in our history; rather, it is a dynamic construction of moving particles constrained by a few fundamental forces. It is also a world with large differences in density, temperature, and types of material. The combination of mobile, interactive atoms that are distributed nonuniformly provides the basis for the rich variety of phenomena observed in our universe, from exploding stars to the evolution of life.

One would assume that an understanding of macroscopic phenomena occurring in such a universe should require a corresponding understanding of the atomic level phenomena. In many cases this assumption, although true, is not of much importance. For instance, the forces between large objects are clearly the residuals of the forces between the atoms with which they are made, but it is seldom useful to pursue this. However, there are many macroscopic phenomena for which the atomic behavior does play a fundamental, controlling role and an understanding of the atomic level dynamics is important. In passing, we note that the study of the atomic and molecular basis of macroscopic phenomena has always been strongly linked to notions of scientific reductionism by the nonscientific community. This was a special concern because atoms and molecules are the building blocks for biology and hence life. Much of the general resistance to the idea of trying to understand our world by reducing it to its building blocks is justified, as there often has been an accompanying lack of sensitivity toward larger issues. However, part of the opposition is a matter of style. It is based on the mistaken notion that the description of the behavior of atoms is not an art form, when in fact it clearly is. Although this text will obviously place a heavy emphasis on the quantitative aspects of the description, I hope the reader will also obtain a feeling for the qualitative aspects, the envisaging of "unseen" phenomena that is the art of physics.

In this chapter some problem areas that require an understanding of atomic and molecular collisions will be considered. The discussion will be primarily descriptive and we will return to treat some of these same phenomena quantitatively in the last chapter. This discussion also should clarify which problems will and will not be treated in the text. Put simply, the primary emphasis will be on the collisions and interactions of ions, atoms and molecules, and the heavy particles. Attention will be paid to the result of these interactions, like the production of photons and electrons from excitations and ionization of the atoms. Similarities and differences between heavy-particle collisions and collisions involving incident electrons will be considered and examples involving incident electrons will be used at certain points in the text. I will ignore primary events initiated by photons and changes in the nuclear structure of the atoms although secondary events involving the ions or electrons produced will be treated. Finally, nonrelativistic velocities only will be considered. Although the following presentation is necessarily simplified, it is hoped that the important collisional information required will be clear and the similarities between disparate research areas will be evident.

## Radiation Cascades

When radiations (particles or photons) from an outside source impinge on and penetrate into a material, various observable phenomena occur that are a direct result of a chain of events referred to as a radiation cascade. For instance, when the sun shines on the atmosphere, the concentrations of chemical species change and an ionized region appears that reflects radio waves. Likewise, a source of fast particles, like a nuclear reactor, can cause embrittlement of the container or general damage to the surrounding materials, including the inactivation of biological materials. In both cases the initial radiation loses intensity as it passes through the material and initiates new radiation within the material.

In the first example, the constituents of the atmosphere are ionized by ultraviolet light, creating a plasma of ions and fast electrons. These photoelectrons are in turn slowed, transferring their energy to the atmospheric constituents and, in the process, cause further excitations and ionizations. The excited atoms and molecules eventually emit photons of lower frequency, hence the initial photons are responsible for a cascade of electrons and lower-energy photons. The ions created in the process also initiate a series of events, referred to as chemical reactions. These processes will be considered shortly.

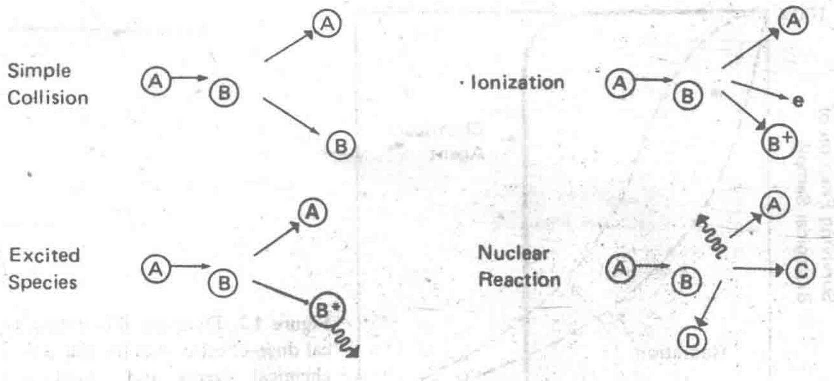

**Figure 1.1.** Events that occur frequently when atoms collide.

Changes in the structure of materials subjected to fast heavy-particle radiation, like alpha particles, protons, or neutrons, can be understood as a series of collision events of the incident particles with the atoms of the target material. The fast moving, incident particles in these collisions transfer kinetic energy to a number of target atoms and, in addition, may ionize or excite these atoms and even initiate a nuclear reaction. Therefore, a single collision event can produce fast heavy particles, referred to as secondaries, electrons, or photons, as shown in Figure 1.1. If a secondary atom or ion is excited in a very dense material (e.g., a solid), it may lose its internal energy in a subsequent collision with another target atom. Very high energy photons, x-rays and $\gamma$-rays, are often produced in materials when the tightly bonded, inner-shell electrons of heavy atoms are removed or when nuclear reactions are initiated. These high-energy photons may also produce additional ionization and, hence, electrons. Therefore, the incident particles initiate two separate cascades—secondary electrons and fast heavy particles. The embrittlement of material, which is one result of such a cascade, is caused primarily by displacement damage, the knocking out of place of target particles. On the other hand, the damage to biological materials is mostly due to the cascade of ionization events set up by the secondary electrons and high-energy photons. Radiation cascades are also used to modify the nature of a material, by implanting incident atoms, and to remove layers of a material, by "knocking off" or sputtering the surface atoms.

The biological case is worth pursuing as a means of understanding the relationship between initial radiation events and final macroscopic effects. In considering the effect of high-energy radiation on cells (or the biological constituents of the cell: DNA, RNA, and various enzymes), the simplest question one asks is: What happens to a cell after it receives a given quantity of radiation?

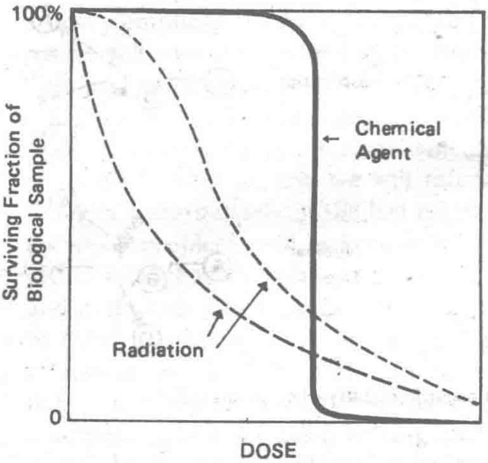

**Figure 1.2.** Diagram illustrating typical dose–effect curves for the action of chemical agents and radiation [cf. K. G. Zimmer, *Studies on Quantitative Radiation Biology*, Oliver & Boyd, Edinburgh and London (1961)].

Dose–response curves of the type shown in Figure 1.2 clearly indicate the causal nature of radiation damage, which is different in nature from damage induced by administering chemical agents for which there is a clear threshold. Simply relating damage to dose, although useful as an initial attempt at radiation protection, is limited by the distinctiveness and distribution of the initial energy-absorbing events between, for instance, processes initiated by $\gamma$-rays and $\alpha$-particles. To simplify the problem, it is customary to subdivide the set of events initiated by the radiation into various stages, associating approximate characteristic times with the events occurring at each stage, as shown in Table 1.1.

The characteristic times shown in Table 1.1 indicate that, although a chemical reaction can occur, in a probabilistic sense, during the absorption of the radiation, the relative slowness of these reactions means it is highly unlikely. The reactions occur in response to the background milieu of broken bonds and ionizations and are not dependent *directly* on the type of radiation. The effect of the type and energy of the radiation will determine only the initial state of the material. In the first two stages indicated, the material is in a very nonequilibrium state. When thermal equilibrium of moving particles is established locally, chemical reaction kinetics involving reactive radicals dominates the material transformations. Finally, the "permanent" chemical alterations can be slowly repaired, resulting in cell alterations, or even be amplified by biological processes. In the following, we discuss the mathematical description of the physical stage for a biological or physical material in which the atomic constituents can be considered randomly ordered and the incident radiation is a fast ion. The discussion is intended to make clear the collision parameters needed for modeling this problem.

To describe a radiation cascade, we imagine dividing a uniformly ir-

**Table 1.1.** Events Initiated by Radiation

| | |
|---|---|
| | Incident radiation |
| | ↓ |
| Physical stage, $\leq 10^{-13}$ sec | Energy absorption (radiation cascade) |
| | ↓ |
| | Excited and ionized molecules |
| | ↓ |
| Physicochemical stage, $\sim 10^{-10}$ sec | Rearrangements (intermolecular energy transfer) |
| | ↓ |
| | Primary lesions and diffusible radicals |
| | ↓ |
| Chemical stage, $\sim 10^{-6}$ sec | Production of bioradicals (secondary reactions) |
| | ↓ |
| | Molecular alterations |
| | ↓ |
| Biological stage, ~ seconds to years | Biological alterations and repair |

radiated material into thin slabs. At each depth fast primaries and secondaries enter and leave the slab, as shown in Figure 1.3, at rates to be determined. These rates are obtained by applying a rather obvious conservation principle. That is, the difference between the radiation intensity entering and leaving the slab must be due to sources or sinks of radiation *within* the slab. For instance, an ion traversing the slab may collide with an atom, losing some of its momentum and setting the target atom in motion, which is now added to the flux of particles.

We define $I_i(\mathbf{p}, z)d^3p$ to be the intensity of particle radiation of type $i$,

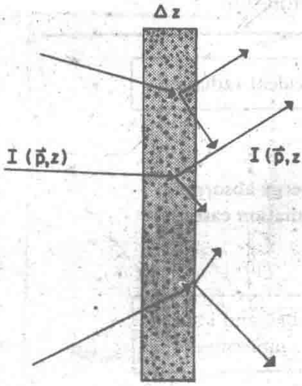

**Figure 1.3.** Collision cascade. Events leading to a change in the flux of particles of various momenta in a slab of thickness $\Delta z$.

with momenta between $\mathbf{p}$ and $\mathbf{p}+d\mathbf{p}$ at the depth $z$ [i.e., $I_i(\mathbf{p}, z)d^3p$ is the number of particles per unit area per unit time having momenta between $\mathbf{p}$ and $\mathbf{p}+d\mathbf{p}$ crossing a unit surface perpendicular to $\mathbf{p}$]. The change in intensity in a slab involves a decrease due to interaction of the incident radiation with the target particles and an increase due to any newly created particles of the same type and momentum. We can define a quantity $\omega_i(\mathbf{p}, \mathbf{p}')$ to be the probability per unit path length of a particle of type $i$ and momentum $\mathbf{p}$ changing to a momentum between $\mathbf{p}'$ and $\mathbf{p}'+d\mathbf{p}'$ in passing through a thin slab. The change in intensity in crossing the slab is

$$\Delta I(\mathbf{p}) = -\text{Loss}\,(\mathbf{p}\rightarrow\mathbf{p}') + \text{Gain}\,(\mathbf{p}''\rightarrow\mathbf{p}) + \text{Sources} \tag{1.1}$$

In Appendix E the transport equation for a radiation cascade is constructed using Eq. (1.1). The resulting integro-differential equation for the intensity at depth $z$ of radiation of type $i$ has the form

$$\cos\theta\,\frac{\partial I_i}{\partial z}(\mathbf{p}, z) = -\int [I_i(\mathbf{p}, z)\omega_i(\mathbf{p}, \mathbf{p}') - I_i(\mathbf{p}', z)\omega_i(\mathbf{p}', \mathbf{p})]\,d^3p' + \mathscr{S}_i(\mathbf{p}, z) \tag{1.2}$$

where $\cos\theta \equiv \hat{p}\cdot\hat{z}$ accounts for the difference between the direction of motion and the penetration direction. On the left of Eq. (1.2) is the change in the intensity of the radiation; on the right are the loss and gain due to scattering, where the integral indicates a sum over all possible changes in momenta. The $\mathscr{S}_i$ accounts for all other sources and sinks and obviously contains a considerable amount of the physics of processes occurring in materials. A similar equation can be constructed for each type of radiation in the cascade, and these equations will not be independent.

To solve Eq. (1.2), in addition to specifying boundary conditions, one has to describe $\mathscr{S}_i$ and $\omega_i(\mathbf{p}, \mathbf{p}')$ for each type of particle. This means that one has to calculate or measure the occurrence probability of all collisions or energy-loss events that might occur in the material, a formidable task. What is clear immediately is that $\mathscr{S}_i$ and $\omega_i(\mathbf{p}, \mathbf{p}')$ are proportional to the target number density. That is, more events will occur per unit path length if the targets are closely spaced. If the targets are all the same, and one defines the number of targets per unit volume as $n_T$, then $\omega(\mathbf{p}, \mathbf{p}')\, d^3p/n_T$ has the dimensions of area, and is referred to as the collision cross section for scattering with a change in the momentum from $\mathbf{p}$ to $\mathbf{p}'$. This is a quantity we will consider in detail throughout the text. A simple loss mechanism or source term, $\mathcal{S}_i$, occurs if, in addition to scattering, the material provides an overall drag force on the radiation, as is the case for charged-particle radiation. Writing the energy loss per unit path length for an atom of type $i$ and momentum $\mathbf{p}$ moving through the atomic electrons as $(dE/ds|_e)_i$, referred to as the electronic stopping power, we have

$$\mathcal{S}_i(\mathbf{p}, z) = -\left(\left|\frac{dE}{ds}\right|_e\right)_i \frac{d}{dE} I_i(\mathbf{p}, z) \tag{1.3}$$

The intensity, $I_i(\mathbf{p}, z)$, tells the state of the cascade at any $z$. For example, if $\omega_i^b(\mathbf{p})$ is the probability per unit path length of producing a broken bond by a particle of type $i$ and momentum $\mathbf{p}$, then the distribution of broken bonds per unit path length is calculated using $I_i$:

$$\sum_i \int I_i(\mathbf{p}, z)\omega_i^b(\mathbf{p})\, d^3p$$

In Eq. (1.4), we have summed over all particle types in the cascade and all momenta. Source terms like $\mathcal{S}_i$ or $\omega_i^b$, which are also collision related, form part of the subject matter of the text.

In the process of describing the cascade by solving for $I_i(\mathbf{p}, z)$, it is easy to lose track of the eventual goal, which is to predict or understand the possible macroscopic results of the cascade. Although the relationship between the initial set of events and the final result is often not clear, describing the cascade, and the immediate results of the cascade, is an important first step, and already much progress has been made in describing the latter stages. For irradiation-induced changes in physical materials, the situation is somewhat simpler. The physical stage is followed by a chemical stage in which the vacancies produced and atoms implanted migrate thermally until equilibrium is established, resulting in a material with new properties or structural damage.

## Gas Dynamics

The description of the thermal behavior of gases was the first significant success of the atomic model of matter. This is most vividly characterized via Boltzmann's description of entropy, a quantity which is a direct result of the statistical nature of a universe composed of large numbers of small, mobile, identical components. Although the science of thermodynamics, without the explicit reference to the atomic nature of matter, is a well-understood art in its own right, the fact that its laws can be founded on atomic dynamics is important. It is important not only because of the statistical basis of the laws, but also because the atoms and molecules themselves have structure which produces deviations in even the simplest thermodynamic behavior. For instance, the van der Waals correction to the ideal gas law depends on the size of the atoms of the gas and the fact that they distort somewhat as they collide.

Whereas in our previous example we considered a directed beam on a material, the more general case of a random thermal flux entering a material is also important. The diffusion of gases through materials, including other gases, has been of continuing interest both as a means for separating gases, like the different isotopes of $UF_6$, and as a mechanism for the distribution of gases in the upper atmospheres of planets. Diffusion is a result of density and/or temperature gradients acting as thermodynamic driving forces. Conserving particles in any volume element of the gas, we give the continuity equation for diffusion in a stationary medium, shown in Appendix E to be

$$\frac{\partial}{\partial t} n_i + \nabla(n_i \mathbf{w}_i) = P_i - L_i \tag{1.5}$$

where $n_i$ is the density of species $i$, $\mathbf{w}_i$ the mean transport velocity, and $P_i$ and $L_i$ are the production and loss terms. If over a reasonable period of time the average value of $n_i$ at each position remains static, the time-independent form of Eq. (1.5),

$$\nabla(n_i \mathbf{w}_i) = P_i - L_i \tag{1.6}$$

is seen to be related to the earlier time-independent transport equation for a cascade, Eq. (1.2). That is, $n_i \mathbf{w}_i$ is an average flux of particles, $(P_i - L_i)$ is the source/sink term, and the collision term in Eq. (1.2) averages to zero because of the random nature of the particle motions.

The mean flux of particles can be determined from the conservation of momentum. Defining a frictional drag force on the particles proportional to $\mathbf{w}_i$, we write the change in momentum of the particles per unit volume, when $\nabla \cdot \mathbf{w}_i = 0$, as

$$\frac{d}{dt}(m_i n_i \mathbf{w}_i) = -\nu_i(m_i n_i \mathbf{w}_i) + \mathbf{f}_i \tag{1.7}$$

where $m_i$ is the mass of the particles; $\nu_i$ is the collision frequency, which indicates the resistance to flow; $f_i$ is the force per unit volume, if any, acting on the particles; and the time derivative is a total time derivative $d/dt =$