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Sincerely,

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Oxford University Press

November 1, 1995

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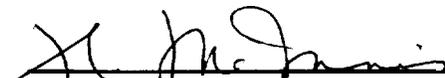
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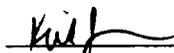
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1/24/97

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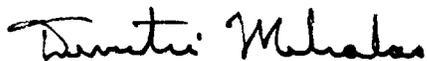
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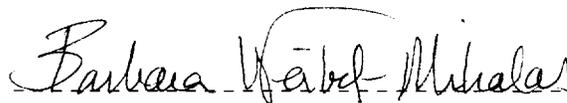
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Foundations of
Radiation Hydrodynamics

Dimitri Mihalas & Barbara Weibel Mihalas

Foundations of
Radiation Hydrodynamics

Foundations of
Radiation Hydrodynamics

Dimitri Mihalas

Barbara Weibel Mihalas
High Altitude Observatory
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Sacramento Peak Observatory

To the memory of our fathers, Emmanuel Demetrious Mihalas and Emil Edwin Weibel, who helped us set our standards, and with homage to Thomas Stearns Eliot, whose inspiring words:

> All men are ready to invest their money
> But most expect dividends.
> I say to you: *Make perfect your will.*
> I say: take no thought of the harvest,
> But only of proper sowing.

have given us the courage to try to attain them.

Preface

This book is the result of our attempt, over the past few years, to gather the basic tools required to do research on radiating flows in astrophysics. The subject of radiation hydrodynamics is very large and cuts across many disciplines in physics and astronomy: fluid dynamics, thermodynamics, statistical mechanics, kinetic theory, and radiative transfer, to name a few. The relevant material is scattered widely among a large number of books, journal papers, and technical reports; indeed, some of it exists only as folklore among practitioners in the field. As a result it has been difficult for both students and research scientists to do productive work in this area with a clear understanding of the full significance of the assumptions they have made, of how their work relates to other problems, and without having to reinvent techniques already in use.

In writing this book our primary goal has been to expose the great foundation-stones of the subject, and to erect upon them solid, if incomplete, walls of methodology on which others can later build. Accordingly, we have quite deliberately concentrated on fundamentals, and have limited severely the discussion of applications to only a few examples whose purpose is to instruct, to illustrate a point, or to provoke deeper thought.

The book divides naturally into three parts; throughout we have attempted to keep the discussion self-contained. In the first part, comprising Chapters 1 to 5, we focus on the dynamics of *nonradiating fluids*, both ideal and real, classical and relativistic, and then consider applications to a few astrophysically interesting problems: waves, shocks, and stellar winds. As an illustration of numerical methods we outline the basic von Neumann–Richtmyer technique for one-dimensional Lagrangean hydrodynamics. While many of these topics are covered in other books, it is nevertheless necessary to develop them here to the level of completeness, and with the particular emphasis, required to make a meaningful connection to the theory of *radiating fluids*.

The second part of the book, Chapters 6 to 8, deals with the physics of radiation, radiation transport, and the dynamics of radiating fluids. Here we have attempted to emphasize the very close relationship of radiation hydrodynamics to ordinary fluid dynamics, and to display the underlying unity and strong parallelism of the two formalisms. We therefore approach radiation hydrodynamics as the study of a composite fluid, consisting of

material particles and photons. We develop both the continuum and kinetic-theory views for both matter and radiation, exploiting the conceptual advantages of each in order to paint a complete picture of the physics of the composite radiating fluid. An essential difference between the dynamics of radiating and nonradiating fluids is that because photons typically have much longer mean free paths than their material counterparts (perhaps approaching or exceeding the physical size of the entire flow), they can introduce a fundamental global coupling between widely separated parts of the flow, which must be treated by a full transport theory. We have attempted to counter what seems to be a commonly held opinion that radiation transport theory is an arcane art, accessible only to specialists, by arguing that conceptually it is simply a nonlocal kinetic theory for a special class of particles (photons) that do not experience body forces but interact strongly with the material component of the fluid locally, while being responsive to the global properties of the flow. We have found this paradigm to be extremely fruitful for our own thinking. Furthermore, we have attempted to show how radiation transport fits naturally into fluid-dynamical computations, in particular how a fully Lagrangean treatment of radiation transport can be incorporated into numerical calculations of one-dimensional flows in both the diffusion and transport regimes. Finally, we discuss a few illustrative examples of astrophysical flows in which radiation plays an important role.

The third part of the book is a short appendix on tensor calculus. We have found that many astronomers and physicists working on radiation hydrodynamics problems are unfamiliar with tensor techniques, and therefore cannot appreciate the power, beauty, and deep physical insight they afford. In the text we exploit tensor concepts to write equations that are covariant by inspection, an approach that allows one to make the transition from ordinary fluids, to relativistic fluids, to radiation almost automatically. The appendix summarizes only the basic material used in the text, and we assume that our readers have this minimum background. Those who do not should read the appendix first; the effort will be amply repaid.

The theory developed in this book has a wide range of application, including such diverse astrophysical phenomena as waves and oscillations in stellar atmospheres and envelopes, nonlinear stellar pulsation, stellar winds, supernova explosions, accretion flows onto compact objects, the initial phases of the cosmic expansion, and many others. It also has direct application in other areas, for example to the physics of laser fusion and of reentry vehicles. Since our professional backgrounds are those of solar/stellar astronomers we have focused almost exclusively on stellar-oriented applications. We have limited the discussion by choice to relatively low-energy phenomena, and by necessity mainly to one-dimensional flows. Even with these restrictions the essential physics of the problem emerges clearly. We hope that this book will serve as a useful starting point and as a guide to a larger literature.

We wish to acknowledge with sincere thanks the helpful contributions of many colleagues, too numerous to list here. We particularly thank Dr. John I. Castor, who understands radiation hydrodynamics better than anyone else we know, for sharing his insights with us, and for helping us learn much of what we know about the subject. We thank Dr. Robert P. Weaver for offering constructive suggestions and asking penetrating questions, which have clarified both our thinking and our writing; we are especially grateful for his unrelenting insistence that we always keep the physics in the foreground. We also thank Dr. J. Robert Buchler for several stimulating and illuminating exchanges of ideas. In addition, one of us (D. M.) thanks Drs. Robert W. Selden and Keith A. Taggart of Los Alamos National Laboratory for hospitality and financial support during the summers of 1981 and 1982 when portions of this book were written and revised.

Finally, we wish to thank Kathleen Welch and Paulina Franz for conscientiously producing a beautiful typescript.

Boulder, Colorado   D.M.
January, 1984   B.W.M.

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Foundations of
Radiation Hydrodynamics

1

Microphysics of Gases

The material component of the astrophysical fluids that we consider in this book is typically a dilute gas composed of single atoms, ions, and free electrons. Insofar as we are interested in the large-scale dynamical behavior of this compressible fluid in response to imposed external forces (both gravitational and radiative), it often suffices to view the gas as a continuum and to describe it in terms of macroscopic properties such as pressure, density, temperature, etc., along with certain macroscopic transport coefficients that specify energy and momentum transport within the gas itself (i.e., thermal conduction and viscosity effects). But when we seek actually to calculate these macroscopic properties and their relationships with one another, particularly when the gas is not in equilibrium or when it interacts with a radiation field, we must examine its microscopic properties in detail and develop appropriate models on an atomic scale. In this chapter we therefore discuss the microphysics of gases from three distinct points of view, each of which complements the others, and all of which yield useful information. Throughout this chapter we ignore radiation, returning to its effects in Chapter 6.

A very basic macroscopic description of gases is afforded by the theory of *thermodynamics.* Although it is possible to develop such a theory within a purely axiomatic framework [see, e.g., (**C1,** Chap. 1)] we shall instead regard it as the formal expression of empirical results obtained from astute experimentation. An alternative description is provided by *kinetic theory,* in which one develops a model of the gas as a system of individual particles interacting according to prescribed laws of force. In the end the results of kinetic theory can be no better than our knowledge of the laws of interaction among the constituent particles (and our ability to solve the equations that result from these laws), and are, in this sense, model dependent. But, in practice, this theory gives a remarkably accurate account of the behavior of real gases even for manifestly crude atomic models. A rather different approach, in some ways more powerful than the preceding ones, is taken by classical *statistical mechanics,* by which we can calculate the most probable state of a gas under prescribed external conditions and evaluate all of its properties quite completely in terms of fundamental atomic constants and an irreducible set of thermodynamic parameters. We obtain this complete picture, however, only for gases in

equilibrium. In contrast, despite its dependence on a definite (and usually oversimplified) atomic model, kinetic theory permits one to treat *non-equilibrium* gases in regimes where both thermodynamics and statistical mechanics provide little, if any, information. Thus it is apparent that it will repay our efforts to consider each of these approaches in turn.

Even though most astrophysical fluids are composed of several chemical species, for the purposes of developing the basic theory we shall confine attention to a pure hydrogen gas and consider mixtures of elements only where required in specific applications. By doing so we can treat all the essential phenomena (e.g., ionization) but still enjoy expository simplicity while obtaining equations in their least complicated form. Furthermore, we shall show that it is usually adequate to describe a gas by a single set of macroscopic parameters (e.g., temperature) despite the fact that the gas may be composed of at least three rather different constituents (atoms, ions, and electrons). Finally, on the spatial scales of interest here we can usually ignore *plasma* properties and view the gas as an electrically neutral, single-component (in the sense just mentioned) material. Extensive discussions of multicomponent gases can be found in (**B1**), (**C4**), and (**H1**), while plasma properties are treated in some detail in (**C4,** Chap. 19), (**K1**), and (**S2**).

1.1 Thermodynamics

1. *Equation of State of a Perfect Gas*

The force exerted by a gas on the walls of a container is directed along the outward normal to the containing surface. In the absence of external forces acting on the gas, it will exert the same force per unit area, the *pressure p,* on all points of the walls. Experiment shows that the pressure exerted by a gas at constant temperature is inversely proportional to its *volume V* (Boyle's law), and that the pressure exerted by a fixed volume of gas is directly proportional to its thermodynamic *temperature T* (the law of Charles and Gay-Lussac). These results are combined into an *equation of state* for a *perfect gas,* which states that

$$pV = n\mathscr{R}T, \tag{1.1}$$

where *n* is the number of *moles* of gas present (i.e., the mass of the gas divided by the atomic mass of its constituent particles), and $\mathscr{R}$ is the *universal gas constant.* Equation (1.1) provides an excellent approximation to the behavior of *dilute* (i.e., low-density), gases, the main case we consider in our work; more accurate expressions for imperfect (i.e., real) gases are given in (**H1,** Chaps. 3 and 4).

It has been established experimentally that the number of particles in a mole of gas is a universal constant, *Avogadro's number* $\mathscr{A}_0$; hence *n* moles

contain $n\mathscr{A}_0$ particles. We can therefore rewrite (1.1) as

$$p = NkT \tag{1.2}$$

where N is the number density of particles per unit volume, and $k = \mathscr{R}/\mathscr{A}_0$ is Boltzmann's constant. If the particles in the gas have atomic weight A, then the *density* of the material is $\rho = NAm_{\rm H}$, where $m_{\rm H}$ is the mass of a hydrogen atom. Thus we can write (1.2) alternatively as

$$p = \rho kT/Am_{\rm H} = \rho RT, \tag{1.3}$$

where $R = k/Am_{\rm H}$ is the gas constant for the particular gas being considered. In some applications it is convenient to use the *specific volume* $v = 1/\rho$, the volume per unit mass; (1.3) then becomes

$$pv = RT. \tag{1.4}$$

Equations (1.1) to (1.4) can be used interchangeably, as convenient.

The *state* of a gas is described by *state variables* such as p, ρ, T, etc. One finds empirically (and can show theoretically, cf. §§1.2 and 1.3) that all thermodynamic properties of a gas are specified when the values of any two state variables are given.

2. First Law of Thermodynamics

Experiments show that a gas may exchange energy with its environment by absorbing or releasing heat and by performing mechanical work, and that in such processes an energy conservation principle applies. Consider a *reversible* process, in which the gas is taken infinitely slowly through a sequence of *equilibrium* states, each differing only infinitesimally from its antecedent. Then if $\mathscr{E}$ is the *internal energy* in a volume V of the gas (which we will later see can be identified with the energy of microscopic motions and internal excitation of the particles in the gas), the *first law of thermodynamics* states that

$$d\mathscr{E} = dQ - dW. \tag{2.1}$$

Here dQ is the amount of heat gained or lost (counted positive for gains) and dW is the work done by the gas (counted positive when the gas delivers work to its surroundings) in an infinitesimal process.

We can write dW in terms of state variables because the force exerted by the gas on an element of the container's surface is $\delta\mathbf{F} = p\mathbf{n}\,\delta A$, and thus the work done if the surface moves by an infinitesimal displacement $d\mathbf{x}$ is $\delta(dW) = \delta\mathbf{F}\cdot d\mathbf{x} = p(\mathbf{n}\cdot d\mathbf{x})\,\delta A = p\,\delta V$ where δV is the volume element swept out by δA. Hence, summing over all surface elements,

$$d\mathscr{E} = dQ - p\,dV. \tag{2.2}$$

In terms of the *specific internal energy* e (i.e., internal energy per unit

mass), we have

$$de = dq - p\, d(1/\rho),\qquad(2.3)$$

where dq is the heat input per unit mass.

If in some process the volume changes by a finite amount, then the total work done by the gas is $\Delta W = \int p(V)\, dV$, which clearly depends on the nature of the process, that is, on how p varies with V. We therefore say that dW is an *inexact* differential. In contrast, it is found experimentally that $\mathscr{E}$ for a gas in equilibrium depends only on the state of the gas as defined in §1; hence $\Delta\mathscr{E}$ in any finite process depends only on the values of the state variables in the initial and final states but not on the details of the process between them. We therefore say that $d\mathscr{E}$ is an *exact* differential. It follows that because dW is an inexact differential, dQ must also be an inexact differential.

An *adiabatic* process is one in which the gas exchanges no heat with its surroundings ($dQ \equiv 0$); such processes can be achieved by thermally insulated systems. Consider now the *Joule–Kelvin experiment* in which a perfect gas at temperature T_1, confined to a volume V_1 within a thermally insulated container, is allowed to expand adiabatically into an additional volume V_2 initially containing a vacuum. It is found empirically that the final temperature of the gas is again T_1. In this process $\Delta Q \equiv 0$ (adiabatic) and $\Delta W \equiv 0$ (because the gas meets no resistance in its expansion and therefore does no work); therefore by the first law $\Delta\mathscr{E} \equiv 0$. In general, we can write $\mathscr{E} = \mathscr{E}(T, V)$; but we have just shown that $\Delta\mathscr{E}$ is zero for arbitrary ΔV at fixed T, hence we reach the important conclusion that, for a perfect gas, $\mathscr{E}$ is a function of T only [see also equation (5.5)].

If an input of heat dQ into a system induces a temperature-change dT, we define the *heat capacity* C as

$$C \equiv (dQ/dT).\qquad(2.4)$$

This quantity depends on the amount of material present; it is more useful to work with the *specific heat c*, the heat capacity per unit mass, given by

$$c \equiv (dq/dT).\qquad(2.5)$$

If the volume of the gas is unchanged during the delivery of dq, we have the *specific heat at constant volume* c_v; similarly, if the pressure is unchanged we have the *specific heat at constant pressure* c_p.

A large number of useful relations can be deduced directly from the first law (2.3) by choosing different sets of state variables. Because any thermodynamic variable can be expressed in terms of any other two, in calculating derivatives it is helpful to employ a notation of the form $(\partial z/\partial x)_y$ to indicate that (x, y) are the independent variables chosen, and that y is being held constant in the calculation of the derivative of z with respect to x. Now suppose that we have any three variables (x, y, z) connected by a functional relation $F(x, y, z) = 0$, in which any two of the variables may be

considered to be independent. Then it is straightforward to derive [see, e.g., (**S1,** §3–3)] the important relations

$$(\partial x/\partial y)_z = 1/(\partial y/\partial x)_z \tag{2.6}$$

and

$$(\partial x/\partial y)_z (\partial y/\partial z)_x (\partial z/\partial x)_y = -1. \tag{2.7}$$

Furthermore, if w is a function of any two of (x, y, z), then

$$(\partial x/\partial y)_w (\partial y/\partial z)_w = (\partial x/\partial z)_w. \tag{2.8}$$

Suppose now that we choose (T, ρ) as the independent variables. Then

$$de = (\partial e/\partial T)_\rho \, dT + (\partial e/\partial \rho)_T \, d\rho, \tag{2.9}$$

hence from (2.3),

$$dq = (\partial e/\partial T)_\rho \, dT + [(\partial e/\partial \rho)_T - (p/\rho^2)] \, d\rho. \tag{2.10}$$

In a process at constant volume $d\rho \equiv 0$ and $dq = c_v \, dT$; therefore

$$c_v = (\partial e/\partial T)_\rho. \tag{2.11}$$

This result is completely general. For a process at constant pressure $dq = c_p \, dT$, and in view of (2.11), we have

$$c_p = c_v + [(\partial e/\partial \rho)_T - (p/\rho^2)](\partial \rho/\partial T)_p. \tag{2.12}$$

For adiabatic processes $dq \equiv 0$, therefore

$$c_v (\partial T/\partial \rho)_s = [(p/\rho^2) - (\partial e/\partial \rho)_T], \tag{2.13}$$

where the subscript s indicates the derivative at constant entropy (cf. §3).

These results can be cast into a standard form by using the following definitions. Write the *coefficient of thermal expansion* of the gas as

$$\beta \equiv (\partial \ln v/\partial T)_p = -(\partial \ln \rho/\partial T)_p, \tag{2.14}$$

its *coefficient of isothermal compressibility* as

$$\kappa_T \equiv -(\partial \ln v/\partial p)_T = (\partial \ln \rho/\partial p)_T, \tag{2.15}$$

and its *coefficient of adiabatic compressibility* as

$$\kappa_s \equiv -(\partial \ln v/\partial p)_s = (\partial \ln \rho/\partial p)_s. \tag{2.16}$$

Then (2.9) and (2.10) become

$$(\partial e/\partial \rho)_T = (p/\rho^2) - (c_p - c_v)/\beta\rho \tag{2.17}$$

and

$$(\partial T/\partial \rho)_s = (c_p - c_v)/\beta\rho c_v. \tag{2.18}$$

Suppose now we take (p, T) as the independent variables. Then

$$de = (\partial e/\partial T)_p \, dT + (\partial e/\partial p)_T \, dp \tag{2.19}$$

and

$$d\rho = (\partial\rho/\partial T)_p \, dT + (\partial\rho/\partial p)_T \, dp, \tag{2.20}$$

so that (2.3) becomes

$$dq = [(\partial e/\partial T)_p - (p/\rho^2)(\partial\rho/\partial T)_p] \, dT + [(\partial e/\partial p)_T - (p/\rho^2)(\partial\rho/\partial p)_T] \, dp. \tag{2.21}$$

By considering a process at constant pressure we find

$$c_p = (\partial e/\partial T)_p - (p/\rho^2)(\partial\rho/\partial T)_p; \tag{2.22}$$

a process at constant volume implies

$$c_v = c_p + [(\partial e/\partial p)_T - (p/\rho^2)(\partial\rho/\partial p)_T](\partial p/\partial T)_\rho; \tag{2.23}$$

and an adiabatic process implies

$$c_p(\partial T/\partial p)_s = (p/\rho^2)(\partial\rho/\partial p)_T - (\partial e/\partial p)_T. \tag{2.24}$$

Using (2.6) and (2.7) we can rewrite (2.22) to (2.24) into the standard forms

$$(\partial e/\partial T)_p = c_p - \beta p/\rho, \tag{2.25}$$

$$(\partial e/\partial p)_T = \kappa_T[(p/\rho) - (c_p - c_v)/\beta] \tag{2.26}$$

and

$$(\partial T/\partial p)_s = \kappa_T(c_p - c_v)/\beta c_p. \tag{2.27}$$

Finally, choosing (p, ρ) as independent variables we find by a similar analysis

$$(\partial e/\partial p)_\rho = \kappa_T c_v/\beta, \tag{2.28}$$

$$(\partial e/\partial\rho)_p = (p/\rho^2) - c_p/\beta\rho, \tag{2.29}$$

and

$$(\partial p/\partial\rho)_s = c_p/\kappa_T\rho c_v. \tag{2.30}$$

The *specific enthalpy* of a substance is defined as

$$h = e + pv = e + (p/\rho). \tag{2.31}$$

Thus

$$dh = de + p \, d(1/\rho) + dp/\rho, \tag{2.32}$$

so from the first law (2.3) we have

$$dq = dh - dp/\rho. \tag{2.33}$$

We then see that for a process at constant pressure we have, quite generally,

$$c_p = (\partial h/\partial T)_p. \tag{2.34}$$

Comparing (2.34) with (2.11), we see that enthalpy plays the same role in

isobaric processes that internal energy does in processes at constant volume.

3. Second Law of Thermodynamics

The first law of thermodynamics is insufficient by itself to provide a complete theory for thermodynamics. From practical experience, it is found that certain physical processes cannot actually be realized despite the fact that they conserve energy. In general terms, one finds that in certain processes energy may be channeled into forms in which it becomes effectively unrecoverable from the gas as useful work or as heat that can be transferred to its surroundings. In a sense the energy has been *degraded*; in fact, the energy has been dissipated at the molecular level by processes that result in a more highly disordered system. We return to this point in §11.

These empirical findings are summarized into a *second law of thermodynamics*, which may be stated in several equivalent forms. For our purposes it is most direct to introduce a state function S, called the *entropy* of the system, defined such that if the system exchanges an amount of heat dQ with a reservoir at a temperature T in a reversible process, then

$$dS \equiv dQ/T. \tag{3.1}$$

The second law is equivalent to the statement that in *any* cyclic transformation, the following inequality holds:

$$\oint \frac{dQ}{T} \leq 0 \tag{3.2}$$

where the integral is evaluated over the entire cycle.

Consider now a reversible cycle. Let the system traverse the cycle in one direction, and let $dQ_1(T)$ denote the heat received in the process. Now reverse the cycle, and consider a new cycle with $dQ_2(T) \equiv -dQ_1(T)$. In both cases the material starts and ends in the same state. Now because (3.2) holds for *any* cycle we must simultaneously have

$$\oint \frac{dQ_1(T)}{T} \leq 0 \tag{3.3a}$$

and

$$\oint \frac{dQ_2(T)}{T} = -\oint \frac{dQ_1(T)}{T} \leq 0, \tag{3.3b}$$

whence we see that for a reversible cycle

$$\oint_{rev} \frac{dQ}{T} = 0. \tag{3.4}$$

We can now show that dS is a perfect differential, and hence that the entropy difference between two states is independent of the nature of the

reversible processes connecting those states. Thus let A and B be two definite states at chosen points on a reversible cycle, and let path 1 denote a process leading from A to B and path 2 a different process leading from B back to A. Then by (3.4),

$$\oint \frac{dQ}{T} = \left(\int_A^B \frac{dQ}{T} \right)_1 + \left(\int_B^A \frac{dQ}{T} \right)_2 = 0. \tag{3.5}$$

But by (3.1),

$$\left(\int_A^B \frac{dQ}{T} \right)_1 = S(B) - S(A), \tag{3.6}$$

hence from (3.5)

$$S(B) - S(A) = -\left(\int_B^A \frac{dQ}{T} \right)_2 = \left(\int_A^B \frac{dQ}{T} \right)_2, \tag{3.7}$$

which shows that the entropy difference is path independent, as stated.

Consider now an *irreversible* process I joining states A and B. Follow this process by a reversible process R that returns the system from B to A in a cycle. From (3.2) we then have

$$\int_I \frac{dQ}{T} + \int_R \frac{dQ}{T} \le 0, \tag{3.8}$$

or

$$\int_I \frac{dQ}{T} \le \left(-\int_B^A \frac{dQ}{T} \right)_R = \left(\int_A^B \frac{dQ}{T} \right)_R = S(B) - S(A), \tag{3.9}$$

the equality holding only if I were reversible.

We can now prove that the entropy of an isolated system must always increase. In such a system $dQ \equiv 0$ (because the system is isolated from its surroundings), and hence from (3.9) we immediately have

$$S(B) \ge S(A), \tag{3.10}$$

the equality holding only if all processes occurring were to be reversible. But all natural processes are actually irreversible, for they always take place at a finite rate with finite departures from a sequence of perfect equilibrium states. Thus the entropy content of a natural system tends always to increase, and a thermally isolated system will therefore ultimately find itself in equilibrium in the state of maximum entropy consistent with imposed external constraints.

In terms of entropy we can rewrite the first law for a reversible process as

$$T \, dS = d\mathscr{E} + p \, dV \tag{3.11}$$

or

$$T \, ds = de + p \, d(1/\rho) \tag{3.12}$$

where s is the *specific entropy*.

4. Thermal Properties of a Perfect Gas

For a perfect gas we can derive explicit expressions for the thermodynamic variables; in practice these are extremely useful because we can often approximate astrophysical fluids as perfect gases. We recall that the Joule–Kelvin experiment implies that for a perfect gas the internal energy $e = e(T)$, hence from (2.11) we have an exact relation

$$e = \int c_v \, dT. \tag{4.1}$$

From kinetic theory we will find that for a perfect gas c_v is a constant, hence

$$e = c_v T, \tag{4.2}$$

where we suppress an additive constant.

Now, using (1.3) in (2.14) and (2.15), we find the thermal expansion coefficient is

$$\beta = 1/T \tag{4.3}$$

and the isothermal compressibility is

$$\kappa_T = 1/p. \tag{4.4}$$

Then from (2.17) we immediately obtain the important relation

$$c_p = c_v + (\beta p/\rho) = c_v + R. \tag{4.5}$$

The *ratio of specific heats* for a perfect gas is the constant

$$\gamma \equiv (c_p/c_v) = 1 + (R/c_v). \tag{4.6}$$

From kinetic theory we shall find $\gamma = \frac{5}{3}$ for a perfect monatomic gas.

The specific enthalpy for a perfect gas follows from (2.31), (4.2), and (4.5) as

$$h = c_v T + RT = c_p T. \tag{4.7}$$

The specific entropy of a perfect gas can be calculated directly from (4.2), (3.12), (2.11), and (1.3), which imply

$$ds = c_v (dT/T) - R(d\rho/\rho). \tag{4.8}$$

Or, in view of (4.5),

$$ds = c_p (dT/T) - R(dp/p). \tag{4.9}$$

Thus

$$s = s_0 + c_v \ln T - R \ln \rho \tag{4.10}$$

or

$$s = s_0' + c_p \ln T - R \ln p. \tag{4.11}$$

We cannot evaluate the constants in (4.10) and (4.11) from thermodynamic

considerations alone; they can be calculated explicitly using statistical mechanics, cf. §12.

Now consider an adiabatic change for a perfect gas. From (4.8) and (4.5) we have

$$c_v \, d(\ln T) = (c_p - c_v) \, d(\ln \rho), \tag{4.12}$$

or

$$T = T_0(\rho/\rho_0)^{\gamma-1}. \tag{4.13}$$

Equivalent forms of (4.13) are

$$p = p_0(\rho/\rho_0)^\gamma \tag{4.14}$$

and

$$p = p_0(T/T_0)^{\gamma/(\gamma-1)}. \tag{4.15}$$

From (4.13) to (4.15) we see why γ is called the *adiabatic exponent*. Relations of the form (4.13) to (4.15) are called *polytropic laws;* they can be generalized to cases other than perfect gases [see §19 and §56 below, and (**C5**, Chaps. 9 and 12)].

Finally, from (2.16) and (4.14), we have, for the adiabatic compressibility of a perfect gas,

$$\kappa_s = 1/\gamma p. \tag{4.16}$$

5. Some Consequences of the Combined First and Second Laws

A great many useful results can be derived from the combined first and second laws for reversible processes as expressed by (3.12), along with the fact that dS is an exact differential. Thus suppose we expand de as in (2.9) to obtain

$$ds = T^{-1}(\partial e/\partial T)_\rho \, dT + T^{-1}[(\partial e/\partial \rho)_T - (p/\rho^2)] \, d\rho. \tag{5.1}$$

Now because ds is exact we know that we can also write

$$ds = (\partial s/\partial T)_\rho \, dT + (\partial s/\partial \rho)_T \, d\rho, \tag{5.2}$$

and we thereby conclude that

$$(\partial s/\partial T)_\rho = T^{-1}(\partial e/\partial T)_\rho \tag{5.3}$$

and

$$(\partial s/\partial \rho)_T = T^{-1}[(\partial e/\partial \rho)_T - (p/\rho^2)]. \tag{5.4}$$

Moreover, $(\partial^2 s/\partial T \, \partial \rho) \equiv (\partial^2 s/\partial \rho \, \partial T)$; hence from (5.3) and (5.4) we obtain

$$(\partial e/\partial \rho)_T = [p - T(\partial p/\partial T)_\rho]/\rho^2 = [p - (\beta T/\kappa_T)]/\rho^2, \tag{5.5}$$

where we have used (2.6), (2.7), (2.14), and (2.15). In particular, for a perfect gas, we now see from (4.3) and (4.4) that $(\partial e/\partial \rho)_T \equiv 0$, hence $e \equiv e(T)$, in agreement with the Joule–Kelvin experiment.

From the first law alone we were able to derive (2.12), giving a relation between c_v and c_p; but now in light of (5.5) we can rewrite this result as

$$c_p - c_v = -(T/\rho^2)(\partial p/\partial T)_\rho (\partial \rho/\partial T)_p. \tag{5.6}$$

Or, using (2.6), (2.7), (2.14), and (2.15), we have the general expression

$$c_p - c_v = \beta^2 T/\kappa_T \rho. \tag{5.7}$$

From experiment we find that $\kappa_T > 0$ for most substances, hence (5.7) implies that $(c_p - c_v) \geq 0$ for most materials, a result that follows directly from kinetic theory and statistical mechanics.

From (5.3), (5.4), and (5.5) we see that by taking (ρ, T) as independent we have

$$(\partial s/\partial T)_\rho = c_v/T \tag{5.8}$$

and

$$(\partial s/\partial \rho)_T = -\beta/\kappa_T \rho^2, \tag{5.9}$$

and thus

$$T\,ds = c_v\,dT - (\beta T/\kappa_T \rho^2)\,d\rho. \tag{5.10}$$

By a similar analysis, one finds by taking (p, T) as independent

$$(\partial e/\partial p)_T = (\kappa_T p - \beta T)/\rho, \tag{5.11}$$

$$(\partial s/\partial T)_p = c_p/T, \tag{5.12}$$

$$(\partial s/\partial p)_T = -\beta/\rho, \tag{5.13}$$

and

$$T\,ds = c_p\,dT - (\beta T/\rho)\,dp. \tag{5.14}$$

Finally, by taking (ρ, p) as independent we find

$$(\partial s/\partial p)_\rho = \kappa_T c_v/\beta T, \tag{5.15}$$

$$(\partial s/\partial \rho)_p = -c_p/\beta \rho T, \tag{5.16}$$

and

$$T\,ds = (\kappa_T c_v/\beta)\,dp - (c_p/\beta \rho)\,d\rho. \tag{5.17}$$

1.2 Kinetic Theory

6. The Distribution Function and Boltzmann's Equation

We can gain a much deeper insight into the physical properties of gases by forsaking the macroscopic picture of thermodynamics and developing in its place a microscopic kinetic theory. We restrict attention to a gas composed of a single species of particle. A macroscopic sample of gas typically contains an enormous number of particles; for example, in a stellar atmosphere the characteristic particle density is $N = 10^{16}\,\text{cm}^{-3}$. Such large numbers immediately show that there is no hope (nor any point) in our

attempting to develop an exact particle-by-particle description of the system, but instead that we require a *statistical* picture that gives the distribution of particles in space and over velocity.

The large particle density quoted above implies that the average distance between particles is quite small: $d_0 = (4\pi N/3)^{-1/3} \approx 3 \times 10^{-6}$ cm for $N \sim 10^{16}$. This spacing is very large, however, compared to a typical particle size, which we can estimate to be of the order of a Bohr radius $a_0 = 5 \times 10^{-9}$ cm; these numbers imply that the particles occupy only about a part in 10^8 of the volume available to them. The interparticle spacing is also very much larger than the de Broglie wavelength $\lambda = h/p \approx h/\sqrt{3mkT}$ associated with each particle; for example, for atomic hydrogen at $T = 10^4$ K, $\lambda \approx 2 \times 10^{-9}$ cm, so that $\lambda \ll a_0 \ll d_0$.

Furthermore, if density fluctuations in the medium are random, the fractional root-mean-square fluctuation in a macroscopic volume, say 1 cm^3, is very small: $\delta N/N = N^{1/2}/N = N^{-1/2}$. For example, in a stellar atmosphere, a characteristic scale of interest for fluid flow is of the order of 100 km (a pressure scale height) so that even a 1 cm^3 volume with its fractional rms fluctuation of 10^{-8} would be considered minuscule. These numbers show clearly why it is usually reasonable to consider the gas to be a continuum: the smallness of d_0 implies that the material is exceedingly fine grained from a macroscopic view, and the smallness of $N^{-1/2}$ implies that it is extremely smooth.

The considerations outlined above show that to a very high degree of approximation we can consider the gas to be a dilute collection of *classical point particles* (because their wave packets are so highly localized). For electrically neutral particles the interparticle forces are very short range, typically falling off as a large power of the interparticle separation; therefore we can well describe the motion of a typical particle as a sequence of straight-line paths, each interrupted by a brief collision with another particle. Because we view the particles classically, the collision, which is characterized by a collision cross section, can be described by classical mechanics. Furthermore, because the probability of collisions is so small, we can neglect the possibility that three or more particles may collide simultaneously, and can consider only *binary collisions*. As we shall see in §10, the situation is rather different for charged particles interacting by Coulomb forces, which are long range; in that case the dominant contribution comes from large numbers of overlapping weak collisions.

To describe the physical state of the gas statistically, we introduce the *distribution function* $f(\mathbf{x}, \mathbf{u}, t)$ defined such that the average number of particles contained, at time t, in a volume element d^3x about $\mathbf{x}$ and a velocity-space element d^3u about $\mathbf{u}$ is $f d^3x d^3u$. We demand that $f \geq 0$ everywhere (no negative particle densities), and that as $u_i \rightarrow \pm\infty$, $f \rightarrow 0$ sufficiently rapidly to guarantee that a finite number of particles has a finite energy.

Macroscopic properties of the gas are computed from the distribution

function. For example, the particle density is

$$N(\mathbf{x}, t) = \int\!\!\!\int\!\!\!\int_{-\infty}^{\infty} f(\mathbf{x}, \mathbf{u}, t)\, du_1\, du_2\, du_3, \tag{6.1}$$

and the mass density of the material is

$$\rho(\mathbf{x}, t) = A m_{\mathrm{H}} N(\mathbf{x}, t), \tag{6.2}$$

where A is the atomic weight of each particle. Similarly the average velocity of an element of gas (and hence its macroscopic flow velocity) is

$$\mathbf{v}(\mathbf{x}, t) = \langle \mathbf{u} \rangle \equiv N^{-1} \int\!\!\!\int\!\!\!\int_{-\infty}^{\infty} f(\mathbf{x}, \mathbf{u}, t)\mathbf{u}\, du_1\, du_2\, du_3. \tag{6.3}$$

To study the microscopic properties of the gas it is helpful to decompose the particle velocity $\mathbf{u}$ into

$$\mathbf{u} = \mathbf{v} + \mathbf{U}, \tag{6.4}$$

where now $\mathbf{U}$ is the *random velocity* of the particle relative to the mean flow; notice that $\langle \mathbf{U} \rangle \equiv 0$.

We now seek an equation that determines how the distribution function changes in time. For the moment, ignore collisions and assume that the gas particles do not interact. Suppose that at a time t_0 we choose a definite group of particles located in the phase-space volume element $(dx_0, dy_0, dz_0, du_0, dv_0, dw_0)$ around the point $(x_0, y_0, z_0, u_0, v_0, w_0)$. Let the external force acting on these particles be $\mathbf{F}(\mathbf{x}, t)$ so that they experience accelerations $\mathbf{a}(\mathbf{x}, t) = \mathbf{F}(\mathbf{x}, t)/m$, where m is the particle mass. We assume that $\mathbf{a}(\mathbf{x}, t)$ is a smooth function, so that the phase-space element will evolve into a new element (dx, dy, dz, du, dv, dw) centered on the point $\mathbf{x} = \mathbf{x}_0 + \mathbf{u}_0\, dt$ and $\mathbf{u} = \mathbf{u}_0 + \mathbf{a}\, dt$. The phase volume of this new element is related to that of the original by

$$d^3x\, d^3u = J(x, y, z, u, v, w/x_0, y_0, z_0, u_0, v_0, w_0)(d^3x)_0(d^3u)_0 \tag{6.5}$$

where J is the Jacobian of the transformation [cf. equation (A3.3)]. Bearing in mind that (x, y, z) and (u, v, w) are independent sets of variables, we see that

$$J = \begin{vmatrix} 1 & 0 & 0 & dt & 0 & 0 \\ 0 & 1 & 0 & 0 & dt & 0 \\ 0 & 0 & 1 & 0 & 0 & dt \\ (\partial a_x/\partial x)\, dt & (\partial a_x/\partial y)\, dt & (\partial a_x/\partial z)\, dt & 1 & 0 & 0 \\ (\partial a_y/\partial x)\, dt & (\partial a_y/\partial y)\, dt & (\partial a_y/\partial z)\, dt & 0 & 1 & 0 \\ (\partial a_z/\partial x)\, dt & (\partial a_z/\partial y)\, dt & (\partial a_z/\partial z)\, dt & 0 & 0 & 1 \end{vmatrix}. \tag{6.6}$$

Thus $J = 1 + O(dt^2)$, and hence to first order in dt the volume of the phase-space element remains constant, that is,

$$d^3x \, d^3u = (d^3x)_0 (d^3u)_0. \qquad (6.7)$$

Now the number of particles inside the original phase-space element is

$$\delta N_0 = f(\mathbf{x}_0, \mathbf{u}_0, t_0)(d^3x)_0 (d^3u)_0; \qquad (6.8)$$

in the absence of collisions all of these particles end up in the new element, and thus δN_0 must equal δN, where

$$\delta N = f(\mathbf{x}_0 + \mathbf{u}_0 \, dt, \mathbf{u}_0 + \mathbf{a} \, dt, t_0 + dt) \, d^3x \, d^3u. \qquad (6.9)$$

By virtue of (6.7) we therefore find that in the absence of collisions the phase-space density of a group of particles is invariant, that is,

$$f(\mathbf{x}_0 + \mathbf{u}_0 \, dt, \mathbf{u}_0 + \mathbf{a} \, dt, t_0 + dt) = f(\mathbf{x}_0, \mathbf{u}_0, t_0). \qquad (6.10)$$

By expanding to first order in dt we then find

$$(\partial f / \partial t) + u^i (\partial f / \partial x^i) + a^i (\partial f / \partial u^i) = 0, \qquad (6.11)$$

which is known as the *collisionless Boltzmann equation*, or *Vlasov's equation*.

Equation (6.11) holds, of course, only in the absence of collisions and is thus not yet the equation we seek. When collisions occur, their effect is to shuffle particles around in phase space. Thus at $t_1 = t_0 + dt$, some particular particle that was in the original group, but which suffered a collision during the interval dt, will not, in general, find itself within the velocity element d^3u centered around $\mathbf{u} = \mathbf{u}_0 + \mathbf{a} \, dt$, but rather in some other velocity element $(d^3u)'$ centered around some other $\mathbf{u}' \neq \mathbf{u}$. Similarly, other particles not originally in the velocity element $(d^3u)_0$ may suffer collisions during dt that leave them with a final velocity within d^3u. Therefore, when collisions occur, f is no longer invariant, and we must add a source term on the right-hand side of (6.11) which gives the net rate at which particles are shuffled into the phase-space element under consideration. We write this net rate symbolically as $(Df/Dt)_{\text{coll}}$, where we use the Lagrangean time derivative (D/Dt) because we have followed the motion of a particular group of particles in the fluid (cf. §15). Thus the desired equation is

$$(\partial f / \partial t) + u^i (\partial f / \partial x^i) + a^i (\partial f / \partial u^i) = (Df/Dt)_{\text{coll}}, \qquad (6.12)$$

which is known as the *Boltzmann transport equation*.

We must next obtain an explicit expression for $(Df/Dt)_{\text{coll}}$; as will be seen in §7 it can be expressed in terms of an integral over the distribution functions of the collision partners. But before doing that it is well to emphasize that (6.12) provides only an approximation to the physics of real gases. In particular, f is only a *one-particle distribution function*, which is based on the tacit assumption that the probability of finding a particle at a particular point in phase space is independent of the coordinates of all

other particles in phase space. Such a description is inadequate for anything but a dilute gas, and for a system of $\mathcal{N}$ particles the most general description is given by the $\mathcal{N}$-particle distribution function $f_{\mathcal{N}}$, which is defined such that $f_{\mathcal{N}}(\mathbf{x}_1, \ldots, \mathbf{x}_{\mathcal{N}}, \mathbf{u}_1, \ldots, \mathbf{u}_{\mathcal{N}}, t)\, d\mathbf{x}_1 \ldots d\mathbf{x}_{\mathcal{N}}\, d\mathbf{u}_1 \ldots d\mathbf{u}_{\mathcal{N}}$ gives the joint probability of finding the $\mathcal{N}$ particles in phase-space elements

$$(\mathbf{x}_1, \mathbf{x}_1 + d\mathbf{x}_1), \ldots, (\mathbf{x}_{\mathcal{N}}, \mathbf{x}_{\mathcal{N}} + d\mathbf{x}_{\mathcal{N}}), \quad (\mathbf{u}_1, \mathbf{u}_1 + d\mathbf{u}_1), \ldots, (\mathbf{u}_{\mathcal{N}}, \mathbf{u}_{\mathcal{N}} + d\mathbf{u}_{\mathcal{N}}).$$

Notice that $f_{\mathcal{N}}$ depends explicitly on the coordinates of all the particles.

The time evolution of $f_{\mathcal{N}}$ is described exactly by *Liouville's equation*, which determines the continuous trajectory of a point representing the system in an abstract $6\mathcal{N}$-dimensional phase space. In practice it is too difficult to handle the problem with this degree of generality, so Liouville's equation is reduced to a less complicated system of equations known as the *BBGKY hierarchy*. These equations provide a systematic way of treating correlations among particle positions, velocities, and interactions, and thus allow one to describe to various degrees of approximation how a given particle perturbs all others in its vicinity. One can allow for correlations between two, three, or more particles. The BBGKY equations permit one to construct a kinetic theory for dense gases; for further details the reader can consult (**B2**, §10.2) and (**C4**, §16.7). We shall not pursue these approaches further because we will deal exclusively with dilute gases. Boltzmann's transport equation can also be derived directly from Liouville's equation: see (**H1**, 449–452).

7. The Collision Integral

DYNAMICS OF BINARY COLLISIONS

Consider two particles of mass m_1 and m_2 starting from infinity with initial velocities $\mathbf{u}_1$ and $\mathbf{u}_2$, which suffer a collision and move away to infinity with velocities $\mathbf{u}'_1$ and $\mathbf{u}'_2$. Then, because the total momentum of the system comprising both particles is conserved, we have

$$m_1\mathbf{u}_1 + m_2\mathbf{u}_2 = m_1\mathbf{u}'_1 + m_2\mathbf{u}'_2 = (m_1 + m_2)\mathbf{G} \tag{7.1}$$

where $\mathbf{G}$ is the velocity of the center of mass of the system in the laboratory frame. Let $\mathbf{g}_{12}$ and $\mathbf{g}'_{12}$ be the initial and final velocity of particle 1 relative to particle 2, and $\mathbf{g}_{21}$ and $\mathbf{g}'_{21}$ the velocities of particle 2 relative to particle 1, that is,

$$\mathbf{g}_{12} = \mathbf{u}_1 - \mathbf{u}_2 = -\mathbf{g}_{21} \tag{7.2a}$$

and

$$\mathbf{g}'_{12} = \mathbf{u}'_1 - \mathbf{u}'_2 = -\mathbf{g}'_{21}. \tag{7.2b}$$

Then clearly

$$g_{12} = |\mathbf{g}_{12}| = g_{21} \equiv g \tag{7.3a}$$

and

$$g'_{12} = g'_{21} = g'. \tag{7.3b}$$

Using (7.2) in (7.1) we can express the laboratory velocities of the particles in terms of their relative velocities and the center-of-mass velocity:

$$\mathbf{u}_1 = \mathbf{G} - m_2\mathbf{g}_{21}/(m_1 + m_2), \tag{7.4a}$$

$$\mathbf{u}_2 = \mathbf{G} + m_1\mathbf{g}_{21}/(m_1 + m_2), \tag{7.4b}$$

$$\mathbf{u}_1' = \mathbf{G} - m_2\mathbf{g}_{21}'/(m_1 + m_2), \tag{7.4c}$$

$$\mathbf{u}_2' = \mathbf{G} + m_1\mathbf{g}_{21}'/(m_1 + m_2). \tag{7.4d}$$

Thus knowledge of $\mathbf{G}$, $\mathbf{g}_{12}$, and $\mathbf{g}_{12}'$ is equivalent to knowledge of $\mathbf{u}_1$, $\mathbf{u}_2$, $\mathbf{u}_1'$, and $\mathbf{u}_2'$, and vice versa.

In the collision the total energy is conserved, and because the interparticle potential can be set to zero at infinite separation, this is equivalent to the statement that the sum of the initial kinetic energies equals the sum of the final kinetic energies:

$$\tfrac{1}{2}(m_1u_1^2 + m_2u_2^2) = \tfrac{1}{2}(m_1u_1'^2 + m_2u_2'^2). \tag{7.5}$$

Equations (7.1) and (7.5), along with the statement of conservation of mass $(m_1 + m_2 = m_1' + m_2')$ are known as the *summational invariants* of the collision.

Using (7.4) it is easy to show that

$$\tfrac{1}{2}(m_1u_1^2 + m_2u_2^2) = \tfrac{1}{2}(MG^2 + \bar{m}g^2) \tag{7.6a}$$

and

$$\tfrac{1}{2}(m_1u_1'^2 + m_2u_2'^2) = \tfrac{1}{2}(MG^2 + \bar{m}g'^2) \tag{7.6b}$$

where M is the total mass of the system

$$M = m_1 + m_2, \tag{7.7a}$$

and $\bar{m}$ is the *reduced mass*

$$\bar{m} \equiv m_1m_2/(m_1 + m_2). \tag{7.7b}$$

From (7.5) and (7.6) we immediately see that

$$g = g', \tag{7.8}$$

which shows that the relative velocity of the two particles is changed only in direction but not in magnitude by the collision.

A specification of the full three-dimensional trajectories of the particles is a bit complicated [see, e.g., (**V1**, 351–353)], but we do not require this much information and can consider the collision in the plane of the relative orbit of the two collision partners. Assume that the interaction between particles is a *central force*, that is, one that depends only on the magnitude of their separation $x_{12} = |\mathbf{x}_1 - \mathbf{x}_2|$. Let the force exerted by particle 1 on particle 2 be $\mathbf{F}$, and by 2 on 1 be $-\mathbf{F}$; then

$$m_1\ddot{\mathbf{x}}_1 = -\mathbf{F} \tag{7.9a}$$

and

$$m_2\ddot{\mathbf{x}}_2 = \mathbf{F}, \tag{7.9b}$$

so that

$$m_1 m_2 \ddot{\mathbf{x}} \equiv m_1 m_2 (\ddot{\mathbf{x}}_2 - \ddot{\mathbf{x}}_1) = (m_1 + m_2)\mathbf{F}. \tag{7.10}$$

Thus the relative orbit of particle 2 with respect to 1 is identical to the motion of an equivalent particle of mass $\bar{m}$ around a fixed center of force $\mathbf{F}$.

Decomposing (7.10) into radial and tangential components we find

$$\ddot{r} - r\dot{\theta}^2 = F/\bar{m} \tag{7.11a}$$

and

$$r\ddot{\theta} + 2\dot{r}\dot{\theta} = 0. \tag{7.11b}$$

We can integrate (7.11b) straightaway to find *conservation of angular momentum*

$$r^2\dot{\theta} = \text{constant} = gb, \tag{7.12}$$

where b is the *impact parameter* of the collision, that is, the perpendicular distance of particle 1 from the straight-line extension of the incident relative velocity vector $\mathbf{g}$ of particle 2 (see Figure 7.1).

Using (7.12) in (7.11a), and integrating with respect to t after multiplying through by $\dot{r}$, we obtain the energy integral

$$\tfrac{1}{2}(\dot{r}^2 + r^2\dot{\theta}^2) + \phi(r)/\bar{m} = \text{constant} = \tfrac{1}{2}g^2 \tag{7.13}$$

where $\phi(r)$ is the potential energy of the interaction. Suppose now that the interaction can be represented by a power-law potential

$$\phi(r) = C_\alpha/r^\alpha. \tag{7.14}$$

Then using (7.14) in (7.13) and eliminating dt in favor of $d\theta$ via (7.12) we
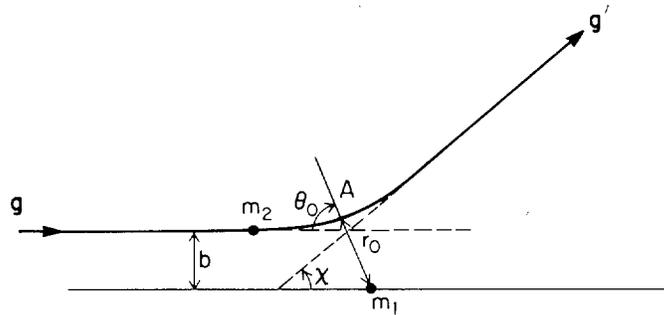
Fig. 7.1 Geometry of binary collision.

obtain the integral

$$
\begin{aligned}
\theta &= \int_R^\infty \left(1 - \frac{2C_\alpha}{\bar{m}g^2 r^\alpha} - \frac{b^2}{r^2}\right)^{-1/2} \frac{b\,dr}{r^2} \\
&= \int_0^{(b/R)} \left[1 - \zeta^2 - \frac{2}{\alpha}\left(\frac{\zeta}{\ell}\right)^\alpha\right]^{-1/2} d\zeta
\end{aligned}
\tag{7.15}
$$

where $\zeta \equiv (b/r)$ and

$$
\ell \equiv b(\bar{m}g^2/\alpha C_\alpha)^{1/\alpha}. \tag{7.16}
$$

Here θ is measured from an axis parallel to the initial asymptote of the orbit. The apse A of the orbit is the point at which $(dr/d\theta) = 0$, which occurs when $R = R_0 = (b/\zeta_0)$ where ζ_0 is the largest root of the equation

$$
1 - \zeta_0^2 - (2/\alpha)(\zeta_0/\ell)^\alpha = 0. \tag{7.17}
$$

When $R = R_0$, θ achieves the value θ_0 shown in Figure 7.1; the angle of deflection χ between the asymptotes is the supplement of twice θ_0, hence

$$
\chi(\ell) = \pi - 2 \int_0^{\zeta_0} [1 - \zeta^2 - (2/\alpha)(\zeta/\ell)^\alpha]^{-1/2} \, d\zeta. \tag{7.18}
$$

Equations (7.16) to (7.18) show that χ depends on b, g, and the interparticle potential only through the parameters α and ℓ.

THE COLLISION CROSS SECTION

The rate at which collisions occur can be expressed in terms of a collision cross section. Suppose the initial velocities of the particles are $\mathbf{u}_1$ and $\mathbf{u}_2$; these suffice to fix the center of mass velocity $\mathbf{G}$, the relative velocity $\mathbf{g}$, and the orientation of the plane of the relative orbit. The initial velocities do not completely fix the properties of the collision, however, because they do not determine the impact parameter b, which must therefore be taken as an independent variable. When b is also given, the collision is uniquely determined.

Choose a particle to act as a collision center and bombard it with an incident flux of particles; let $\mathcal{I}$ be the number of particles in the incident beam crossing a unit area normal to the beam in a unit time. Then the rate of collisions having impact parameters on the range $(b, b + db)$ within an increment $d\varepsilon$ of azimuthal angle (see Figure 7.2) is $R_1 = \mathcal{I}b\,db\,d\varepsilon$. Alternatively we can assign to the process a *differential cross section* $\sigma(g, \chi)$, defined such that the rate at which particles are scattered out of the incident beam into an increment of solid angle $d\Omega$ around some direction $\mathbf{n}'$ specified by the angles (χ, ε) is $R_2 = \mathcal{I}\sigma(g, \chi)\,d\Omega$. But R_1 and R_2 refer to the same particles. Therefore noting that $d\Omega = \sin \chi\,d\chi\,d\varepsilon$ we conclude that

$$
\sigma(g, \chi) = b\,|\partial b/\partial \chi|/\sin \chi. \tag{7.19}
$$
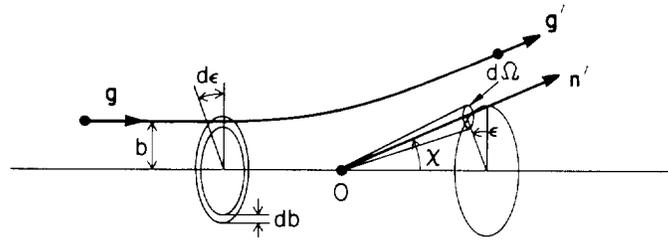
Fig. 7.2 Scattering from a collision center.

Another useful notation for the cross section is $\sigma = \sigma(\mathbf{u}_1, \mathbf{u}_2; \mathbf{u}_1', \mathbf{u}_2')$ because the initial and final velocities together are sufficient to determine the collision uniquely. In calculating collision rates we may write either $\sigma\, d\Omega$ or the differential target area $b\, db\, d\varepsilon$, as convenient.

For the important case of power-law interactions we find from (7.16) and (7.19) that

$$\sigma(g, \chi)\, d\Omega = (\alpha C_\alpha/\bar{m})^{2/\alpha} g^{-4/\alpha}\ell\, d\ell\, d\varepsilon. \qquad (7.20)$$

Another extremely useful model is to imagine that the particles are *rigid elastic spheres* of diameter d that interact only on contact. In this case, if θ_0 is the angle of the point of contact relative to the incident path, then $b = d \sin \theta_0$, and $\chi = \pi - 2\theta_0$ (see Figure 7.3) so that from (7.19)

$$\sigma = \tfrac{1}{4}d^2, \qquad (7.21)$$

which is independent of both the relative speed g and the deflection angle χ of the collision partner. Despite the extreme simplicity of this model, it actually yields useful estimates of collision rates, mean-free-paths, and transport coefficients, and we shall employ it in later work.
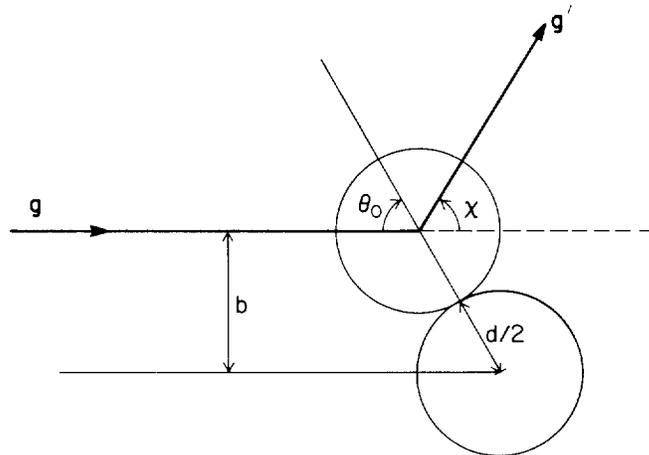
Fig. 7.3 Collision of two rigid spheres.

In addition to the differential cross section itself, various angular moments of the cross section will appear in later developments. The *total cross section* is

$$\sigma_T = \sigma_{(0)} \equiv \oint \sigma \, d\Omega = \int_0^{2\pi} d\varepsilon \int_0^{\pi} \sigma \sin \chi \, d\chi = 2\pi \int_0^{\pi} \sigma \sin \chi \, d\chi. \quad (7.22)$$

For rigid spheres we find

$$\sigma_T(\text{rigid sphere}) = \pi d^2, \quad (7.23)$$

which is clearly just the geometrical cross section of the two colliding particles. For power-law interactions (7.22) diverges, hence classically the total cross section is infinite; convergence of the integral is, however, obtained when quantum-mechanical effects are taken into account (**W2**, 9).

The transport coefficients for viscosity and thermal conductivity are related to the moment

$$\sigma_{(2)} \equiv \oint \sigma \sin^2 \chi \, d\Omega = 2\pi \int_0^{\pi} \sigma \sin^3 \chi \, d\chi. \quad (7.24)$$

For rigid spheres

$$\sigma_{(2)} = \tfrac{2}{3}\pi d^2. \quad (7.25)$$

For power-law interactions

$$\sigma_{(2)} = 2\pi(\alpha C_\alpha/\bar{m})^{2/\alpha} g^{-4/\alpha} A_2(\alpha), \quad (7.26)$$

where

$$A_2(\alpha) \equiv \int_0^{\infty} \sin^2 \chi(\ell)\ell \, d\ell \quad (7.27)$$

is a pure number tabulated in (**C4**, 172) for various values of $\nu \equiv \alpha + 1$.

The differential collision cross section has certain important invariance properties:

(a) Time reversal. If we reverse the sense of time (i.e., run the collision backward) each particle must merely retrace its original trajectory. Therefore

$$\sigma(\mathbf{u}_1, \mathbf{u}_2; \mathbf{u}_1', \mathbf{u}_2') = \sigma(-\mathbf{u}_1', -\mathbf{u}_2'; -\mathbf{u}_1, -\mathbf{u}_2). \quad (7.28)$$

(b) Rotation and reflection. Let $\mathbf{u}^\dagger$ denote the vector obtained from $\mathbf{u}$ by transformation under a rotation of the coordinate axes in space, or under a reflection with respect to a given plane, or both. Because the collision event depends only on the magnitudes and *relative* orientations of $\mathbf{u}_1$, $\mathbf{u}_2$, $\mathbf{u}_1'$, $\mathbf{u}_2'$ it is obviously unaffected by these transformations, hence we must have

$$\sigma(\mathbf{u}_1, \mathbf{u}_2; \mathbf{u}_1', \mathbf{u}_2') = \sigma(\mathbf{u}_1^\dagger, \mathbf{u}_2^\dagger; \mathbf{u}_1'^\dagger, \mathbf{u}_2'^\dagger). \quad (7.29)$$

(c) Inverse collisions. The *inverse* of a collision is defined to be the collision obtained by interchanging $(\mathbf{u}_1, \mathbf{u}_2)$ with $(\mathbf{u}_1', \mathbf{u}_2')$. As shown in
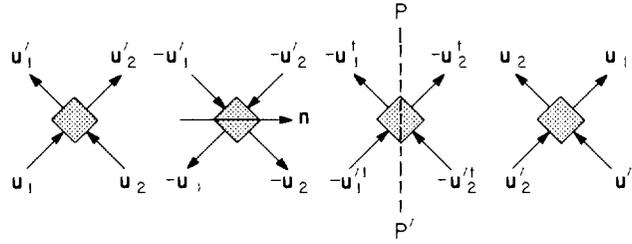
Fig. 7.4 Invariance properties of binary collisions.

Figure 7.4, the inverse collision can be obtained from the direct collision by a combination of a time reversal, followed by a 180° rotation about an axis **n** perpendicular to the center-of-mass momentum $M\mathbf{G}$, and then by a reflection through a plane PP' perpendicular to **n**. It follows from (7.28) and (7.29) that direct and inverse collisions necessarily have the same cross section:

$$\sigma(\mathbf{u}_1, \mathbf{u}_2; \mathbf{u}_1', \mathbf{u}_2') = \sigma(\mathbf{u}_1', \mathbf{u}_2'; \mathbf{u}_1, \mathbf{u}_2). \tag{7.30}$$

BASIC FORM OF THE COLLISION INTEGRAL

We are now in a position to evaluate the collision term $(Df/Dt)_{\text{coll}}$ in (6.12). Label target particles in the phase-element considered with the subscript "1" and their collision partners with the subscript "2". We calculate first R_{out}, the rate at which particles of type 1 are scattered out of the phase-space element $d^3x_1\, d^3u_1$. For each particle of type 1, the number of particles of type 2 moving with velocities on the range $(\mathbf{u}_2, \mathbf{u}_2 + d\mathbf{u}_2)$, incident within a range of impact parameters $(b, b + db)$ and within azimuth range $d\varepsilon$ in a unit time, is $(f_2\, d^3u_2)gb\, db\, d\varepsilon$, where g is the incident speed of particles 2 relative to particle 1, and for brevity we have written $f_2 \equiv f_2(\mathbf{x}, \mathbf{u}_2, t)$. The total number of collisions is obtained by summing over all impact parameters, azimuths, and incident velocities, and then multiplying by the number of particles of type 1 present, namely $f_1\, d^3x_1\, d^3u_1$. Thus

$$R_{\text{out}}\, d^3x_1\, d^3u_1 = -\left(\int\int\int f_1 f_2 gb\, db\, d\varepsilon\, d^3u_2\right) d^3x_1\, d^3u_1. \tag{7.31}$$

In calculating R_{out} we have tacitly made the assumption of *molecular chaos*, that is, that both sets of particles are independently distributed according to f without any correlation between velocity and position or location of other particles.

Next we calculate R_{in}, the rate at which particles not originally within the phase-space element $d^3x_1\, d^3u_1$ are scattered into that element. We now wish to consider only those collisions whose result is a particle moving with velocity $\mathbf{u}_1$ within d^3u_1 *after* the collision. This is most simply done by

considering inverse encounters of the form $(\mathbf{u}_1', \mathbf{u}_2') \rightarrow (\mathbf{u}_1, \mathbf{u}_2)$. By an argument similar to that used above we find

$$R_{in} \, d^3x_1 \, d^3u_1 = \left(\int\int\int f_1' f_2' g' b \, db \, d\varepsilon \, d^3u_2' \right) d^3x_1 \, d^3u_1' \qquad (7.32)$$

where $f_1' \equiv f(\mathbf{x}, \mathbf{u}_1', t)$ and $f_2' \equiv f(\mathbf{x}, \mathbf{u}_2', t)$.

Equation (7.32) can be cast into a more useful form by noticing that $d^3u_1 \, d^3u_2 \equiv d^3u_1' \, d^3u_2'$, which can be proved as follows. From (7.4) we know that we can express $(\mathbf{u}_1, \mathbf{u}_2)$ in terms of $(\mathbf{G}, \mathbf{g})$; hence we can write

$$d^3u_1 \, d^3u_2 = J(\mathbf{u}_1, \mathbf{u}_2/\mathbf{G}, \mathbf{g}) \, d^3G \, d^3g, \qquad (7.33)$$

where J is the Jacobian of the transformation. From (7.4) we find

$$J = \begin{vmatrix} 1 & -m_1/(m_1 + m_2) \\ 1 & m_2/(m_1 + m_2) \end{vmatrix} \equiv 1. \qquad (7.34)$$

Therefore, $d^3u_1 \, d^3u_2 = d^3G \, d^3g$. Similarly we can express $(\mathbf{u}_1', \mathbf{u}_2')$ in terms of $(\mathbf{G}, \mathbf{g}')$ and write

$$d^3u_1' \, d^3u_2' = J' \, d^3G \, d^3g' = d^3G \, d^3g' \qquad (7.35)$$

because one finds $J' \equiv 1$. But $\mathbf{G}$ is unchanged by the collision, and from (7.8) $g = g'$ because the relative velocity changes only in direction. Therefore $d^3G \, d^3g' \equiv d^3G \, d^3g$, which in turn implies from (7.33) and (7.35) that $d^3u_1' \, d^3u_2' = d^3u_1 \, d^3u_2$. Using this result and (7.8) we can thus rewrite (7.32) as

$$R_{in} \, d^3x_1 \, d^3u_1 = \left(\int\int\int f_1' f_2' g b \, db \, d\varepsilon \, d^3u_2 \right) d^3x_1 \, d^3u_1 \qquad (7.36)$$

where now in f_1' and f_2' we consider $\mathbf{u}_1' = \mathbf{u}_1'(\mathbf{u}_1, \mathbf{u}_2)$ and $\mathbf{u}_2' = \mathbf{u}_2'(\mathbf{u}_1, \mathbf{u}_2)$.

The *net* rate of scattering into $d^3x_1 \, d^3u_1$ is simply $(Df_1/Dt)_{coll} = R_{in} + R_{out}$, so that the Boltzmann equation for f_1, accounting for binary collisions, becomes

$$(\partial f_1/\partial t) + u^i(\partial f_1/\partial x^i) + a^i(\partial f_1/\partial u^i) = \int\int\int (f_1' f_2' - f_1 f_2) g b \, db \, d\varepsilon \, d^3u_2,$$

$$(7.37)$$

or, in terms of the differential cross section,

$$(\partial f_1/\partial t) + u^i(\partial f_1/\partial x^i) + a^i(\partial f_1/\partial u^i) = \int\int (f_1' f_2' - f_1 f_2) g \sigma(\mathbf{\Omega}) \, d\Omega \, d^3u_2.$$

$$(7.38)$$

In $\sigma(\mathbf{\Omega})$, $\mathbf{\Omega}$ denotes the angles between $\mathbf{g}$ and $\mathbf{g}'$. From (7.37) and (7.38) we see that the Boltzmann transport equation is a nonlinear integrodifferential equation for the distribution function f; its complicated mathematical nature makes the equation difficult to solve.

ALTERNATE FORMS OF THE COLLISION INTEGRAL

It is convenient to develop here several equivalent forms of moments of the collision integral for later use. Let $Q(\mathbf{u}_1)$ be any function of the particle velocity $\mathbf{u}_1$, and define

$$I \equiv \int \int \int Q(\mathbf{u}_1)(f_1' f_2' - f_1 f_2) g\sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2. \tag{7.39}$$

Suppose now that we merely interchange the labeling 1 and 2 on all particles; obviously the same value of I must result. Adding the two expressions, we see that an equivalent expression for I is

$$I = \tfrac{1}{2} \int \int \int [Q(\mathbf{u}_1) + Q(\mathbf{u}_2)](f_1' f_2' - f_1 f_2) g\sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2. \tag{7.40}$$

Suppose now in (7.40) we replace the collision by its inverse; the integral must have the same value because for every collision there is an inverse collision with the same cross section, and we are thus merely writing two completely equivalent expressions for the sum over all collisions of the value, before the collision, of the function Q. Thus

$$I = \tfrac{1}{2} \int \int \int [Q(\mathbf{u}_1') + Q(\mathbf{u}_2')](f_1 f_2 - f_1' f_2') g'\sigma(\mathbf{\Omega}') \, d\Omega' \, d^3 u_1' d^3 u_2'$$

$$= \tfrac{1}{2} \int \int \int [Q(\mathbf{u}_1') + Q(\mathbf{u}_2')](f_1 f_2 - f_1' f_2') g\sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2, \tag{7.41}$$

where we have used the facts, proven earlier, that $\sigma(\mathbf{\Omega}') = \sigma(\mathbf{\Omega})$, $d\Omega' = d\Omega$, $g' = g$, and $d^3 u_1' \, d^3 u_2' = d^3 u_1 \, d^3 u_2$. Adding (7.40) and (7.41) we have

$$I = -\tfrac{1}{4} \int \int \int [\delta Q(\mathbf{u}_1) + \delta Q(\mathbf{u}_2)](f_1' f_2' - f_1 f_2) g\sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2, \tag{7.42}$$

where

$$\delta Q(\mathbf{u}) \equiv Q(\mathbf{u}') - Q(\mathbf{u}). \tag{7.43}$$

By the same line of argument leading to (7.41), we see that

$$\int \int \int Q(\mathbf{u}_1') f_1 f_2 g\sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2 \equiv \int \int \int Q(\mathbf{u}_1) f_1' f_2' g'\sigma(\mathbf{\Omega}') \, d\Omega' \, d^3 u_1' \, d^3 u_2'$$

$$\equiv \int \int \int Q(\mathbf{u}_1) f_1' f_2' g\sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2. \tag{7.44}$$

Then using (7.44) in (7.39) we see immediately that

$$I = \int \int \int \delta Q(\mathbf{u}_1) f_1 f_2 g\sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2. \tag{7.45}$$

We have shown above that I is unchanged under interchange of $\mathbf{u}_1$ and $\mathbf{u}_2$;

thus, from (7.45), we see that

$$I = \tfrac{1}{2} \int \int \int [\delta Q(\mathbf{u}_1) + \delta Q(\mathbf{u}_2)] f_1 f_2 g \sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2. \qquad (7.46)$$

8. The Maxwellian Velocity Distribution

Boltzmann's equation is quite general and can be applied to a wide variety of physical situations. First, let us suppose that the gas is in a state of *equilibrium*: the material is homogeneous, isotropic, and at rest. The distribution function will then be independent of both position and time, and therefore the number of particles in each velocity class must be constant. If this is to be true when there is a reshuffling of particles by collisions, then it must be possible to pair each collision with its inverse, and we will have *detailed balance*. That is, in equilibrium we must have $(Df/Dt)_{coll} \equiv 0$. We see from (7.37) and (7.38) that this will be the case if

$$f_0(\mathbf{u}_1) f_0(\mathbf{u}_2) - f_0(\mathbf{u}_1') f_0(\mathbf{u}_2') \equiv 0, \qquad (8.1)$$

which is thus a *sufficient* condition for equilibrium; here the subscript zero denotes the equilibrium distribution function. Taking logarithms of (8.1) we have

$$\ln f_0(\mathbf{u}_1) + \ln f_0(\mathbf{u}_2) = \ln f_0(\mathbf{u}_1') + \ln f_0(\mathbf{u}_2'), \qquad (8.2)$$

which states that $\ln f_0$ is a function such that the sum of that function for the two collision partners is conserved in the collision for *any* possible collision. Hence $\ln f_0$ must be expressible as a linear combination of summational invariants.

We saw in §7 that the total mass, momentum, and energy of the collision partners are summational invariants; it is possible to show that these are the *only* linearly independent summational invariants that exist for structureless point particles (**C4**, 50). Therefore we can write f_0 as

$$\ln f_0 = \alpha_1 + \boldsymbol{\alpha}_2 \cdot \mathbf{u} + \alpha_3 u^2 = -\tfrac{1}{2}\beta m (\mathbf{u} - \mathbf{v})^2 + \gamma, \qquad (8.3)$$

where β must be positive to guarantee that $f \to 0$ as $|\mathbf{u}| \to \infty$; the factor $\tfrac{1}{2}m$ was chosen to simplify later results. In (8.3), $\mathbf{v}$ must be the mean velocity defined by (6.3) because the distribution function must be isotropic in the frame in which the material is at rest. Hence, in terms of random velocities $\mathbf{U}$, we have

$$f_0(\mathbf{U}) = A \exp\left(-\tfrac{1}{2}\beta m U^2\right) \qquad (8.4)$$

We can determine the normalization factor in (8.4) by invoking (6.1):

$$N = \int \int \int_{-\infty}^{\infty} f_0(\mathbf{U}) \, d^3 U$$

$$= A \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_{-\infty}^{\infty} \exp(-\tfrac{1}{2}\beta m U^2) U^2 \, dU = A (2\pi/\beta m)^{3/2}, \qquad (8.5)$$

or

$$A = (\beta m/2\pi)^{3/2}N. \tag{8.6}$$

To evaluate β we use $f_0(\mathbf{U})$ to calculate a directly measurable quantity—the pressure. By definition, p equals the momentum transfer from the gas to a wall per unit area per unit time. Erect a perfectly reflecting wall in the (y, z) plane, and confine the gas to the region $x \leq 0$ so that particles hit the wall only if $U_x > 0$. If an incoming particle has velocity (U_x, U_y, U_z), after hitting the wall its velocity is $(-U_x, U_y, U_z)$, and the momentum transferred to the wall is $2mU_x$; the flux of these particles per unit area and time is $U_x f_0(\mathbf{U})$. Therefore the pressure is

$$
\begin{aligned}
p &= \int_{-\infty}^{\infty} dU_z \int_{-\infty}^{\infty} dU_y \int_{0}^{\infty} (2mU_x)U_x A e^{-(\beta m U^2/2)}\, dU_x \\[2mm]
&= mA \int\!\!\!\int\!\!\!\int_{-\infty}^{\infty} U_x^2 e^{-(\beta m U^2/2)}\, d^3U \\[2mm]
&= \tfrac{1}{3}mA \int\!\!\!\int\!\!\!\int_{-\infty}^{\infty} U^2 e^{-(\beta m U^2/2)}\, d^3U \\[2mm]
&= \tfrac{4}{3}\pi mA \int_{-\infty}^{\infty} e^{-(\beta m U^2/2)} U^4\, dU = \frac{mA}{2\pi}\left(\frac{2\pi}{\beta m}\right)^{5/2}.
\end{aligned}
\tag{8.7}
$$

Here we noticed that, by symmetry, the averages $\langle U_x^2 \rangle$, $\langle U_y^2 \rangle$, and $\langle U_z^2 \rangle$ are identical and hence equal to $\tfrac{1}{3}\langle U^2 \rangle$. Now combining (1.2), (8.6), and (8.7) we find $NkT = N/\beta$; therefore

$$\beta = 1/kT. \tag{8.8}$$

The equilibrium velocity distribution, the *Maxwellian distribution*, is thus

$$f_0(\mathbf{U}) = N(m/2\pi kT)^{3/2} \exp(-mU^2/2kT). \tag{8.9}$$

Equations (8.7) to (8.9) can be viewed as giving the definition of the *kinetic temperature*. In equilibrium, the kinetic temperature is identical to the absolute temperature of thermodynamics. But, more important, a kinetic temperature can be uniquely defined by an approach similar to the one above even in situations where the thermodynamic definition can no longer be applied (see §30). We shall therefore take the kinetic temperature as the fundamental operational definition of T in our later work.

The distribution of particles in speed (magnitude of $\mathbf{U}$) is

$$f_0(U)\, dU = N(m/2\pi kT)^{3/2} \exp(-mU^2/2kT)4\pi U^2\, dU. \tag{8.10}$$

The *most probable speed*, at which the maximum of f_0 occurs, is

$$U_{mp} = (2kT/m)^{1/2}; \tag{8.11}$$

the *average speed* is

$$\langle U \rangle = N^{-1} \int_0^\infty U f_0(U) \, dU = (8kT/\pi m)^{1/2}; \tag{8.12}$$

and the *root-mean-square speed* is

$$\langle U^2 \rangle^{1/2} = \left[N^{-1} \int_0^\infty U^2 f_0(U) \, dU \right]^{1/2} = (3kT/m)^{1/2}. \tag{8.13}$$

The distribution function $N^{-1} f_0(U)$ can be factored into the product

$$N^{-1} f_0(U) \, dU_x \, dU_y \, dU_z = [\Phi(U_x) \, dU_x][\Phi(U_y) \, dU_y][\Phi(U_z) \, dU_z] \tag{8.14}$$

where

$$\Phi(U_x) = (m/2\pi kT)^{1/2} \exp(-mU_x^2/2kT), \tag{8.15}$$

and similarly for U_y and U_z. In contrast to f_0, Φ peaks at $U_x = 0$ and by symmetry $\langle U_x \rangle = 0$ (the range being $-\infty \le U_x \le \infty$); as remarked earlier $\langle U_x^2 \rangle^{1/2} = (\langle U^2 \rangle / 3)^{1/2} = (kT/m)^{1/2}$.

The distribution function gives a complete description of the microscopic properties of the gas, hence a knowledge of f_0 is sufficient to derive all macroscopic properties of a gas. For instance, the total translational energy of $\mathcal{N}$ particles is

$$\mathcal{E}_{\text{trans}} = \mathcal{N}(\tfrac{1}{2}m\langle U^2 \rangle) = (\tfrac{3}{2}NkT)V, \tag{8.16}$$

whence we have the important result that for a perfect gas

$$p = \tfrac{2}{3}(\mathcal{E}_{\text{trans}}/V) \equiv \tfrac{2}{3}\hat{e}_{\text{trans}}, \tag{8.17}$$

where $\hat{e}_{\text{trans}}$ denotes the translational energy per unit volume. The translational energy per unit mass is

$$e_{\text{trans}} = \tfrac{3}{2}RT, \tag{8.18}$$

and the energy per particle is $\tilde{e}_{\text{trans}} = \tfrac{3}{2}kT$. The specific enthalpy (per unit mass) is

$$h = e_{\text{trans}} + p = \tfrac{5}{2}RT, \tag{8.19}$$

hence the enthalpy per particle is $\tilde{h} = \tfrac{5}{2}kT$. For a gas of point particles without internal structure (our present model), the total internal energy $\mathcal{E} \equiv \mathcal{E}_{\text{trans}}$ because there are no other modes of energy storage available to the particles; as we shall show in §12 the situation is different for a gas of real atoms.

From (8.18) we see that e_{trans} is a function of T only, as expected from the Joule–Kelvin experiment, and using (2.11) we have

$$c_v = \tfrac{3}{2}R = \tfrac{3}{2}(k/m). \tag{8.20}$$

Hence from (4.5) or (4.11)

$$c_\mathrm{p} = \tfrac{5}{2}R = \tfrac{5}{2}(k/m),\tag{8.21}$$

and therefore

$$\gamma = \tfrac{5}{3}.\tag{8.22}$$

The above results justify the statements made in §4 that c_v, c_p, and γ for a perfect gas are all constants.

Finally, using (8.20) and (8.21) in (4.10) and (4.11), we find that the entropy of a perfect gas is

$$s = s_0 + \tfrac{3}{2}R \ln T - R \ln \rho = s_0' + R \ln T - R \ln p.\tag{8.23}$$

As was true for thermodynamics, kinetic theory is unable to evaluate the additive constants.

Suppose now that we have a *mixture* of gases containing several *non-interacting* chemical species (i.e., particles whose identities do not change when the state of the gas changes); as before, assume the particles have no internal structure. Then

$$N = \sum_s n_s\tag{8.24}$$

where n_s is the number density of particle species s, and

$$\rho = \sum_s \rho_s = m_\mathrm{H} \sum_s n_s A_s\tag{8.25}$$

where A_s is the atomic weight of species s. If the mixture is in equilibrium at a given temperature T, then experiments show that

$$p = \sum_s p_s = \sum_s n_s kT = NkT\tag{8.26}$$

which is *Dalton's law of partial pressures*. Now from (8.16) and (8.17)

$$n_s kT = p_s = \tfrac{2}{3}\hat{e}_s = \tfrac{1}{3}n_s m_s \langle U_s^2\rangle\tag{8.27}$$

which implies that $\tfrac{1}{2}m_s\langle U_s^2\rangle = \tfrac{3}{2}kT$, that is, that all particles have the same amount of kinetic energy (the principle of *equipartition of energy*). Furthermore, we again find that (8.20) to (8.22) hold for c_v, c_p, and γ, and also that the velocity distribution for each species is Maxwellian:

$$f_{(1s}(U_s) = (m_s/2\pi kT)^{3/2} \exp\left(-m_s U_s^2/2kT\right).\tag{8.28}$$

It must be stressed that (8.26) to (8.28) apply only in equilibrium where all particles have the same kinetic temperature. In general, different species of particles may have different kinetic temperatures as defined via equations (8.7) and (8.8); we discuss this question further in §10 where we shall show that the use of a single kinetic temperature is a good approximation in the cases of primary interest to us. Furthermore, when the species can interact "chemically" (e.g., in a gas of atoms, ions, and electrons, where

atoms can ionize to ions plus electrons, and vice versa, or in a relatively cool gas where atoms can form molecules), the internal energy of the mixture contains terms in addition to translational energy, and the expression for e, c_v, c_p, and the adiabatic exponent must be modified (cf. §14).

9. Boltzmann's H-Theorem

We have seen above that (8.1) is a sufficient condition for equilibrium; we shall now prove that it is also a *necessary* condition, and hence that the Maxwellian velocity distribution is the unique equilibrium distribution function. Suppose that the sample of gas is thermally isolated, is homogeneous so that f is independent of $\mathbf{x}$, and that external forces are absent. Consider the functional

$$H(t) \equiv \int f(\mathbf{u}, t) \ln [f(\mathbf{u}, t)] \, d^3 u \qquad (9.1)$$

introduced by Boltzmann. Differentiating with respect to time we have

$$(dH/dt) = \int (1 + \ln f)(\partial f/\partial t) \, d^3 u. \qquad (9.2)$$

Clearly, if $(\partial f/\partial t) \equiv 0$, as it must be for equilibrium, then $(dH/dt) = 0$, which is therefore a necessary condition for equilibrium. We shall show that $(dH/dt) = 0$ implies (8.1), which is thus both necessary and sufficient for equilibrium.

For a uniform gas $(\partial f/\partial x^i) \equiv 0$, and with no external forces $a^i \equiv 0$, so from (7.38)

$$(\partial f/\partial t) \equiv (Df/Dt)_{coll} = \int\int (f_1' f_2' - f_1 f_2) g\sigma(\mathbf{\Omega}) \, d^3 u_2, \qquad (9.3)$$

hence

$$(dH/dt) = \int\int\int (1 + \ln f_1)(f_1' f_2' - f_1 f_2) g\sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2. \qquad (9.4)$$

Then, by virtue of (7.42), we immediately have

$$(dH/dt) = -\tfrac{1}{4} \int\int\int [\ln (f_1' f_2'/f_1 f_2)](f_1' f_2' - f_1 f_2) g\sigma(\mathbf{\Omega}) \, d\Omega \, d^3 u_1 \, d^3 u_2. \qquad (9.5)$$

The integrand in (9.5) is clearly greater than zero whether $(f_1' f_2') < (f_1 f_2)$ or $(f_1' f_2') > (f_1 f_2)$. Therefore,

$$(dH/dt) \le 0, \qquad (9.6)$$

the equality holding only when $f_1' f_2' - f_1 f_2 \equiv 0$.

It can easily be shown that $H(t)$ is bounded from below [see (C4, 67) or (H1, 465)] because the total kinetic energy of an assembly of particles must

be finite. Given this fact and (9.6) we conclude that $H(t)$ continually decreases to some final value, at which point $(dH/dt) = 0$ and we recover (8.1); this proves the necessity and sufficiency of this condition.

Although we have treated $H(t)$ as an arbitrary functional for our present purposes, it has a much deeper physical meaning: it is proportional to the negative of the entropy. We return to this point in §12.

10. The Time of Relaxation

We have shown in §§8 and 9 that the Maxwellian velocity distribution is the unique velocity distribution function for a gas (or mixture of gases) of point particles in equilibrium, and have seen that the physical properties of such gases are easy to calculate. How quickly can this equilibrium state actually be reached by a gas starting with a non-Maxwellian distribution function? This is a question of central importance to our work because when there is fluid flow in the medium, any particular element of material, initially in equilibrium with its surroundings, can be transported to some other position where the ambient conditions differ from its initial conditions. If the characteristic time required to reequilibrate the velocity distribution to a Maxwellian distribution is very short compared to a characteristic flow time, then the gas may be considered to remain locally in equilibrium at each point in the flow because it rapidly accommodates to its slowly varying environment.

From elementary mechanics, we know that, in elastic collisions, energy exchange is most efficient among particles of equal masses, and is inefficient among particles of widely differing masses. It thus comes as no surprise that in a typical astrophysical fluid the longest time scale in the equilibration toward a single Maxwellian velocity distribution is set by energy exchange between the lightest particles (free electrons) and the much heavier atoms and ions. In keeping with our choice of a pure hydrogen gas, let us therefore consider collisions between pairs of charged particles such as electrons with electrons, protons with protons, and electrons with protons.

COULOMB FORCES

Particles with charges Z_1e and Z_2e interact by the Coulomb force

$$F = Z_1Z_2e^2/r^2, \tag{10.1}$$

which, in contrast to forces among neutral particles [where typical values of α in (7.14) are ≥ 5], are extremely long range. A consequence of this long range is that while the force exerted on a test particle falls as r^{-2}, the number of field particles (in a uniform medium) on a range $(r, r + dr)$ rises as r^2, and therefore there will be roughly equal contributions to the collisional interaction from particles at *all* distances. In fact, we shall shortly see that the dominant effect comes from a multitude of weak

collisions with particles at large distances. Because a characteristic collision time is of the order of (b/g), these weak collisions at large b inevitably overlap one another. Therefore the assumptions underlying the binary collision integral in (7.37) and (7.38) break down, and a different approach is indicated.

An alternative expression for the collision integral can be developed by considering changes in a test particle's velocity to be a *Markov process* characterized by a function $P(\mathbf{u}, \Delta\mathbf{u})$, which gives the probability that a particle changes its velocity from $\mathbf{u}$ to $\mathbf{u} + \Delta\mathbf{u}$ in a time interval Δt. On the assumption that weak collisions dominate, $(Df/Dt)_{\text{coll}}$ can then be written in terms of a differential operator containing P and the distribution function f, yielding what is known as the *Fokker–Planck equation*. Derivations of the Fokker–Planck equation from this statistical point of view can be found in (**B2**, §10-9), (**C3**), and (**K1**, §6.3); an in-depth analysis of this equation for an inverse-square force is given in (**R1**). Curiously enough, it is also possible to derive the Fokker–Planck equation directly from the usual Boltzmann collision integral (**C4**, §19.7), despite the radically different physical picture employed in the derivation of that integral.

The Fokker–Planck equation provides a rather complete picture of such important processes as *dynamical friction* (the systematic slowing down of fast-moving particles by drag) and the *diffusion* of particles in phase space (from which the rate of equilibration can be determined). The solution of this equation is, however, complicated, and we shall follow instead a different route by estimating characteristic *times of relaxation* for the equilibration process; a check on these estimates is provided by direct calculations from the Fokker–Planck equation itself (**M1**).

ROUGH CALCULATION OF THE DEFLECTION TIME

A test particle colliding with another particle in the field experiences a change ΔE in its energy and is deflected by an angle χ from its original direction. Because the changes are *random*, we expect that over a long time interval $\langle\Delta E\rangle_T = 0$ and $\langle\chi\rangle_T = 0$. Nevertheless the particle's motion suffers an ever-growing, random-walk departure from the original trajectory, and eventually the particle will be moving on a path essentially unrelated to its original path. We can characterize these cumulative departures by calculating the values of $\sum(\Delta E)^2$ and $\sum\chi^2$ summed over all collisions; because the process is random we expect these sums to grow linearly with time. We can then define an *energy-exchange time* t_E as

$$t_E = E^2 / \{d[\sum(\Delta E)^2]/dt\} \tag{10.2}$$

and a *deflection time* t_D as

$$t_D = 1/(\sum\chi^2)/dt]. \tag{10.3}$$

In the time t_E the energy of a test particle can no longer be considered to

have been even approximately conserved, and thus t_E is a representative time for the velocity distribution to be thermalized towards a Maxwellian. Similarly t_D gives the time required for $\sum (\chi^2)^{1/2}$ to accumulate to about a radian and hence is a representative time over which the velocity distribution becomes isotropized.

Given these definitions, both t_D and t_E can be computed with considerable mathematical precision, but the analysis is intricate [see (**C2,** Chap. 2)]. We therefore give only a heuristic derivation of t_D, which is simple mathematically but retains all the essential physics. Consider a test particle of mass m_1 and charge $Z_1 e$ moving through a field of particles with mass m_2 and charge $Z_2 e$. The integral (7.18) can be evaluated exactly for $\alpha = 1$; one finds

$$\sin \tfrac{1}{2}\chi = [1 + (\bar{m}g^2 b/Z_1 Z_2 e^2)^2]^{-1/2} \tag{10.4}$$

or

$$\tan \tfrac{1}{2}\chi = Z_1 Z_2 e^2 / \bar{m}g^2 b \tag{10.5}$$

where, as in §7, g is the relative speed of the collision partners, b the impact parameter, and $\bar{m}$ the reduced mass defined in (7.7b). Suppose we consider electrons and protons so that $Z = \pm 1$, $\bar{m} \approx m_e$, and $g^2 \approx (3kT/m_e)$, and choose b to be the interparticle spacing $d_0 \sim 3 \times 10^{-6}$ cm quoted in §6. Then, for $T = 10^4$ K, we find that $\chi \approx 4 \times 10^{-2}$ radians. Therefore, a typical encounter results in a small deflection and we can make the approximation

$$\chi(g, b) \approx 2Z_1 Z_2 e^2 / \bar{m}g^2 b. \tag{10.6}$$

Suppose now that the test particle is an electron and the field particles are ions of charge Z_i; then because $m_e \ll m_i$ we can ignore the motions of the field particles, and can also set $\bar{m} = m_e$. If the density of field particles is n_i, then the number of collisions suffered by the test particle in a time t with field particles having impact parameters on the range $(b, b + db)$ is $2\pi n_i g t b\, db$; hence using (10.6) we have

$$\sum \chi^2 \approx 2\pi n_i g t \int_{b_{min}}^{b_{max}} \chi^2(g, b) b\, db = (8\pi Z_1^2 Z_2^2 e^4 n_i t / m_e^2 g^3) \int_{b_{min}}^{b_{max}} b^{-1}\, db$$

$$= (8\pi Z_i^2 e^4 n_i t / m_e^2 g^3) \ln (b_{max}/b_{min}). \tag{10.7}$$

In what follows we shall write $\Lambda \equiv (b_{max}/b_{min})$.

CUTOFF PROCEDURE

The integral over impact parameters in (10.7) diverges at both large and small values of b and therefore two cutoffs must be specified. The divergence for small b is spurious and results from our use of (10.6), which allows $\chi \to \infty$ as $b \to 0$, instead of (10.5), which guarantees that χ remains bounded. A reasonable choice for b_{min} is the value that results in a 90° deflection, that is,

$$b_{min} = Z_i e^2 / m_e g^2. \tag{10.8}$$

The divergence for large b is physical and arises from the long range of the Coulomb interaction, which implies, as described at the beginning of this section, equal contributions from radial shells at *all* distances. But in a real plasma we must have overall charge neutrality, which means that charges of opposite signs surround each other. Therefore, individual field particles at large distances will be partially shielded by charges of opposite sign and will have a diminished effect on the test particle.

We can describe this shielding quantitatively with a theory developed by P. Debye. The probability that a charged particle will be found in a volume element dV is not just $n\,dV$ (where n is the particle density), but depends also on the electrostatic potential ϕ in dV. For example, if $\phi > 0$ at some position, electrons will tend to migrate toward that position while ions will tend to migrate away. We can account for this effect by introducing a Boltzmann factor (cf. §12) which depends on $\psi \equiv (e\phi/kT)$. Then, for electrons, the probability of being located at a point is proportional to

$$\pi_e = \exp{(\psi)} \approx (1 + \psi), \tag{10.9}$$

and for ions

$$\pi_i = \exp{(-Z_i\psi)} \approx (1 - Z_i\psi), \tag{10.10}$$

where we have assumed weak interactions so that $\psi \ll 1$. The average charge density, summing over all ion types, is

$$\rho = e\left(\sum_i n_i Z_i \pi_i - n_e \pi_e\right) = -e\psi\left(n_e + \sum_i Z_i^2 n_i\right). \tag{10.11}$$

Here we have demanded large-scale charge neutrality, which implies that

$$n_e = \sum_i Z_i n_i. \tag{10.12}$$

To calculate the potential around any particular ion we combine (10.11) with *Poisson's equation*

$$\nabla^2 \phi = -4\pi\rho, \tag{10.13}$$

and write

$$\nabla^2 \phi = (\phi/D^2) \tag{10.14}$$

where

$$D \equiv \left\{ kT \Big/ \left[4\pi e^2 \left(n_e + \sum_i Z_i^2 n_i\right) \right] \right\}^{1/2} \tag{10.15}$$

is the *Debye length*. Solving (10.14) for ϕ one obtains $\phi = r^{-1}(Ae^{-r/D} + Be^{r/D})$. Demanding that (1) $\phi \to 0$ as $r \to \infty$, we set $B \equiv 0$; and (2) $\phi \to Z_i e/r$ (the potential of the ion itself) as $r \to 0$, we set $A = Z_i e$. Thus the potential produced by a shielded ion is

$$\phi(r) = (Z_i e/r) \exp{(-r/D)}, \tag{10.16}$$

which shows that charges are effectively completely screened at distances larger than D. Thus, in (10.7), it is reasonable to set $b_{max} = D$. Numerically,

$$D = 4.8(T/n_e)^{1/2} \, \text{cm} \tag{10.17}$$

for a pure hydrogen plasma. For example, in a stellar atmosphere with $T = 10^4$ K, $n_e = 10^{14}$ cm^{-3}, one finds that $D \approx 5 \times 10^{-5}$ cm, which is only about four times r_0, the interparticle spacing.

Collecting results from above we have, for a hydrogen plasma,

$$\Lambda = 3e^{-3}(k^3 T^3/8\pi n_e)^{1/2}. \tag{10.18}$$

Here we have set g^2 in b_{min} equal to $\langle U^2 \rangle = 3kT/m_e$. A table of $\ln \Lambda$ for a hydrogen plasma is given in (**S2,** 73); a typical value for a stellar atmosphere is $\ln \Lambda \approx 10$. Furthermore, for a hydrogen plasma, we obtain

$$t_D \approx m_e^3 g^2/(8\pi e^4 n_p \ln \Lambda). \tag{10.19}$$

We can now justify the claim made earlier that the effects of weak collisions dominate those of strong collisions. The characteristic time between strong collisions (i.e., a 90° deflection) is

$$t_s = 1/(\pi b_{min}^2 n_p g) = m_e^2 g^3/(\pi e^4 n_p). \tag{10.20}$$

Therefore,

$$t_s/t_D \approx 8 \ln \Lambda \tag{10.21}$$

which shows that the weak collisions dominate by two orders of magnitude.

PRECISE EXPRESSIONS FOR THE DEFLECTION AND ENERGY-EXCHANGE TIMES
Equation (10.19) is not rigorous because we have not performed the (complicated) integrations over all angular variables, allowing for the motion of the center of mass, correctly. Exact calculations by Chandrasekhar (**C2,** Chap. 2) show that for a test particle of charge Z_1 and mass m_1, moving with a speed U_1 relative to the velocity centroid of a uniform field of particles having charge Z_2, mass m_2, and an isotropic Maxwellian velocity distribution with dispersion $\langle U_2^2 \rangle = (3kT/m_2)$, the deflection time is

$$t_D = m_1^2 U_1^3/[8\pi e^4 Z_1^2 Z_2^2 n_2 H(x_0) \ln \Lambda] \tag{10.22}$$

and the energy-exchange time is

$$t_E = m_1^2 U_1^3/[32\pi e^4 Z_1^2 Z_2^2 n_2 G(x_0) \ln \Lambda] \tag{10.23}$$

where

$$x_0 \equiv (3/2\langle U_2^2 \rangle)^{1/2} U_1 = (m_2/2kT)^{1/2} U_1. \tag{10.24}$$

The functions $G(x_0)$ and $H(x_0)$ depend on the error function and its derivative; numerical values for $G(x_0)$, $H(x_0)$, and the ratio

$$(t_D/t_E) = 4G(x_0)/H(x_0) \tag{10.25}$$

are listed in Table 10.1. An important point to notice from the table is that

Table 10.1. The functions $G(x_0)$, $H(x_0)$, and the Ratio of Relaxation Times (t_D/t_E)

x_0	$G(x_0)$	$H(x_0)$	(t_D/t_E)	x_0	$G(x_0)$	$H(x_0)$	(t_D/t_E)
0.0	0.0	0.0	2.00	1.5	0.175	0.791	0.89
0.1	0.037	0.075	1.99	1.6	0.163	0.813	0.80
0.2	0.073	0.149	1.98	1.7	0.152	0.832	0.73
0.3	0.107	0.221	1.93	1.8	0.140	0.849	0.66
0.4	0.137	0.292	1.88	1.9	0.129	0.863	0.60
0.5	0.162	0.358	1.81	2.0	0.119	0.876	0.54
0.6	0.183	0.421	1.74	2.5	0.080	0.920	0.35
0.7	0.198	0.480	1.65	3.0	0.056	0.944	0.24
0.8	0.208	0.534	1.56	3.5	0.041	0.959	0.17
0.9	0.213	0.584	1.46	4.0	0.031	0.969	0.13
1.0	0.214	0.629	1.36	5.0	0.020	0.980	0.082
1.1	0.211	0.669	1.26	6.0	0.014	0.986	0.057
1.2	0.205	0.706	1.16	7.0	0.010	0.990	0.041
1.3	0.196	0.738	1.06	8.0	0.008	0.992	0.032
1.4	0.186	0.766	0.97	10.0	0.005	0.995	0.020

t_E is a minimum for $x_0 = 1$, and becomes much larger for particles moving at speeds much above or much below the average speed of the field particles.

THE SELF-COLLISION TIME AND THE EXCHANGE TIME BETWEEN SPECIES

A case of special interest is a group of particles interacting with themselves, for which Spitzer (**S2**) has defined the extremely useful *self-collision time*. For particles having a speed U_1 equal to the rms speed $\langle U_2^2 \rangle^{1/2}$ of their collision partners, $x_0 = (1.5)^{1/2} = 1.225$, and from Table 10.1 we see that $t_D/t_E = 1.14$. Therefore in this case t_D is about equal to t_E and thus provides a good estimate both of the time required to isotropize the velocity distribution and of the time needed for the distribution over energy to approach a Maxwellian. Spitzer denotes this special value of t_D as

$$t_c = m^{1/2}(3kT)^{3/2}/[(8\pi e^4 Z^4 n) \times 0.714 \ln \Lambda] = 11.4(AT^3)^{1/2}/(nZ^4 \ln \Lambda)$$

(10.26)

where A is the atomic weight of the particles in units of the hydrogen mass. A detailed numerical solution of the Fokker–Planck equation shows (**M1**) that in the neighborhood of the average energy the time required for relaxation of a distribution that initially is strongly non-Maxwellian is quite close to t_c as predicted from (10.26). However, the time needed for the distribution to become Maxwellian for energies ranging from zero to several times the average energy is about $10t_c$. Thus t_c provides a semi-quantitative estimate only.

From (10.26) it is immediately obvious that $t_c(\text{protons})/t_c(\text{electrons}) = (m_p/m_e)^{1/2} \approx 43$. The energy-exchange time between electrons and protons follows from (10.23) by choosing $U_1 = (3kT/m_e)^{1/2}$, $m_1 = m_e$, $m_2 = m_p$, $x_0 = (3m_p/2m_e)^{1/2}$, and using the asymptotic formula $G(x_0) \to \frac{1}{2}x_0^2$ for $x_0 \gg 1$. One then finds that the electron–proton energy-exchange time is a factor $(m_p/m_e)^{1/2}$ greater than $t_c(\text{protons})$. Thus

$$t_c(e\text{-}e) : t_c(p\text{-}p) : t_E(e\text{-}p) = 1 : (m_p/m_e)^{1/2} : (m_p/m_e). \qquad (10.27)$$

For a stellar atmosphere with $T = 10^4$ K and $n_e = n_p = 10^{14}$ cm^{-3} one finds from (10.26) and (10.27) that $t_E(e\text{-}p) \approx 10^{-6}$ s. This time may be compared with a characteristic flow time $t_f \sim (l/v)$; in a stellar atmosphere we can take the characteristic length l equal to a scale height $H \approx 100$ km, and the characteristic velocity v equal to the sound speed ≈ 10 km s^{-1}, so that $t_f \sim 10$ s $\sim 10^7 t_E(e\text{-}p)$. Thus, in the absence of any other processes perturbing equilibrium, we conclude that the velocity distribution of all particles in the atmosphere must be quite precisely a Maxwellian at a single kinetic temperature. We shall reexamine this conclusion in §84 where we allow for the effects of recombinations and inelastic collisions between electrons, ions, and atoms.

1.3   Classical Statistical Mechanics

11.   Thermodynamic Probability and Entropy

In classical statistical mechanics, as in kinetic theory, we again deal with an atomic model of the gas (which can now include internal structure of the particles). However, we do not now concern ourselves with the detailed mechanics of collisions among the particles, but instead appeal to certain powerful statistical principles. As before, we make no attempt to follow the time history of particles, but consider instead only the distribution of a large number of particles in the six-dimensional phase space (x, y, z, u_x, u_y, u_z). For the present we assume all the particles are identical and ignore internal structure; we shall relax these restrictions later.

The macroscopic (i.e., thermodynamic) state of the system is completely determined when we specify the total number $\mathcal{N}$ of particles in the system, the volume V they occupy, and their total internal energy $\mathcal{E}$. Associated with this single *macrostate* there will, in general, be an enormous number of *microstates* (i.e., arrangements of particles within phase space), all of which yield the same macroscopic properties. We define the *thermodynamic probability* W to be directly proportional to the number of distinct microstates by which a given macroscopic state can be realized consistent with the constraints implied by specified values of $\mathcal{N}$, V, and $\mathcal{E}$. A fundamental assumption of statistical mechanics is that all microstates are equally probable and that, as a result of collisions, the system continuously evolves from one microstate to another. It then follows that the macrostate

in which we will most probably find the gas is the one that has the largest number of microstates associated with it. As we shall see, there is one particular macrostate for which there are many more microstates than any other, and even small departures from this state are extremely improbable.

A major task of statistical mechanics is the calculation of W. In practice this is done by dividing the available phase volume into elementary *cells*, and then counting the number of ways particles can be distributed into these cells. The details of this procedure will be discussed in §12; here we merely note that the total number of cells, and hence W, is proportional to the total phase volume available.

In principle, statistical mechanics can be constructed without reference to thermodynamics, and a correspondence between the two theories can be made after the fact by an analysis of the relationships among the mathematical expressions that emerge from the development of statistical mechanics. It is simpler, however, to invoke the fundamental connection between thermodynamics and statistical mechanics provided by *Boltzmann's relation*, which states that the entropy S and thermodynamic probability W are related by the expression

$$S = k \ln W \qquad (11.1)$$

where k is Boltzmann's constant.

A complete justification of (11.1) would take us too deeply into the foundations of statistical mechanics and thermodynamics. We can, however, render it plausible by means of a few simple examples and gain useful insight in the process. First, we know from thermodynamics that an isolated system tends toward an equilibrium state of maximum entropy [cf. equation (3.10)]. In statistical terms we expect the system to tend to its most probable state. Boltzmann's relation is consistent with these two statements. It is also in this vein that we can associate entropy with the degree of *disorder* in a system. We can consider a system to be completely ordered if all the particles occupy a single cell in phase space, that is, if all are in the same volume element and move with identical velocities, and hence constitute a unique, perfectly structured, initial configuration. In time, as collisions among particles spread them out in phase space, the entropy rises, the thermodynamic probability increases (because more cells in phase space can be occupied), and at the same time the system becomes more disordered. We may therefore consider entropy to be a quantitative measure of the degree of disorder of a system. Second, suppose we consider the free expansion of a gas into a vacuum (the Joule–Kelvin experiment). We know from experiment that T remains constant in this process, and from (4.10) we have the change in entropy $\Delta S \propto \ln (V_f/V_i)$ where i and f denote "initial" and "final". Thus not only is the process accompanied by an increased uncertainty in our knowledge of the system (because each particle has a larger volume available to it) and hence in its degree of disorder, as expected qualitatively, but also, because $W \propto V$ (i.e.,

the number of available cells), we see that (11.1) is quantitatively just right to describe the process. Third, consider two different gases at the same temperature and pressure, originally separated by a partition in a container. If we remove the partition, T and p remain unaltered, but the gases intermingle, eventually producing a homogeneous mixture through the whole container. Obviously, the degree of disorder of the system has increased. The entropy increase of the system as a whole equals the *sum* of the entropy increases in the two subsystems, $\Delta S = \Delta S_1 + \Delta S_2$. On the other hand, the thermodynamic probability W assigned to the whole system must be proportional to the *product* of the (independent) thermodynamic probabilities of the two subsystems, $W = W_1 \cdot W_2$ (i.e., particles of each gas can independently be distributed through the larger volume). Again one sees that (11.1) provides the correct relation.

Many other examples of the types discussed above can be constructed, but we need not pursue them further because in the final analysis the justification of (11.1) is that it leads to an internally consistent theoretical structure that is in excellent agreement with experiment.

12. Boltzmann Statistics

COUNTING PROCEDURE

Classical statistical mechanics, which is based on *Boltzmann statistics*, can be derived as limiting case of quantum statistics, valid when the number of phase-space cells greatly exceeds the number of particles to be placed in them (i.e., a dilute gas). While this approach affords deep insight [see, e.g., (**H2,** Chaps. 9–12), (**S1,** Chap. 16), (**V1,** Chap. 4)] it is more direct to proceed purely on classical grounds, and to appeal to quantum mechanical concepts only when required.

Our task is now to calculate the number of microstates associated with a given macrostate.

Suppose that we have a fixed number $\mathcal{N}$ of particles within a volume V. We consider these particles to be distributed among cells, each of which has a definite energy ε_i. The number of particles in the ith cell is its *occupation number* ν_i. We agree that all *acceptable* sets of occupation numbers $\{\nu_i\}$ corresponding to the desired macrostate are those $\{\nu_i\}$ such that the total number of particles $\sum \nu_i$ equals the given total number $\mathcal{N}$, and the total energy $\sum \nu_i \varepsilon_i$ equals the given energy $\mathcal{E}$. To obtain the total number of microstates associated with a macrostate we must therefore (1) compute the number of microstates associated with each acceptable set of occupation numbers $\{\nu_i\}$ and then (2) sum over all such sets.

Each energy cell may correspond to several physically different states, all having the same ε_i; such states are called *degenerate*. The number of degenerate states associated with the ith cell is called the *statistical weight* or *degree of degeneracy* g_i of that cell. Having chosen some definite set $\{\nu_i\}$ of occupation numbers that produces the desired macrostate, for purposes

of distributing particles we now discard all empty cells ($\nu_i = 0$), and arrange those with nonzero occupations into a consecutive sequence. We view this sequence as a consecutive set of *partitions* or *boxes*, each of which contains g_i *slots* into which particles can be put.

If we were to assume (as is acceptable classically) that the particles are *distinguishable*, then there are $\mathcal{N}!$ distinct ways we can sort $\mathcal{N}$ particles consecutively into the sequence of partitions, no matter how they are distributed over the slots within each partition. In addition, for each of these $\mathcal{N}!$ sortings, any of the ν_i particles in the ith box can be in any one of the g_i slots available in that box, hence there are $(g_i)^{\nu_i}$ possible ways to arrange ν_i within the ith box. However, each of the $\nu_i!$ permutations of the *order* in which the ν_i particles are inserted into a definite set of slots within the ith box are actually identical, because the particles are, in fact, physically identical (even if we assume that they are distinguishable).

Thus the total number of physically distinct microstates associated with the particular set $\{\nu_i\}$ of occupation numbers is

$$W(\{\nu_i\}) = \mathcal{N}! \prod_i (g_i)^{\nu_i} \Big/ \prod_i \nu_i! \qquad (12.1)$$

Here the products now extend over *all* cells [including empty cells, for which $\nu_i! = 0! = 1$ and $(g_i)^{\nu_i} = (g_i)^0 = 1$].

Using (12.1) one can develop statistical mechanics along the lines described below, and one arrives finally at an expression for the entropy. This expression correctly predicts an increase in entropy if two different gases, originally in volumes V_1 and V_2, respectively, and at the same temperature and pressure, are allowed to mix throughout the entire volume $V = V_1 + V_2$. Unfortunately, it also predicts an entropy increase if the two gases are identical [see (**H1**, §7.6)], which is absurd. This catastrophic result, known as the *Gibbs paradox*, would imply that the entropy of a single homogeneous gas depends on its history (i.e., how many stages of "mixing" have occurred) instead of being a function of the thermodynamic state variables alone. Gibbs showed that the paradox is resolved if we postulate that in (12.1) we have made a counting error of a factor of $\mathcal{N}!$, and that the thermodynamic probability given by a "correct Boltzmann counting" is really

$$W\{\nu_i\} = \prod_i (g_i)^{\nu_i} \Big/ \prod_i \nu_i! \qquad (12.2)$$

Gibbs's ad hoc correction is vindicated by the realization that quantum mechanically the particles are actually indistinguishable; in fact (12.2) is recovered directly from quantum statistics in the limit described at the beginning of this section. We therefore use (12.2) henceforth.

THE EQUILIBRIUM DISTRIBUTION FUNCTION

Summing over all acceptable sets of occupation numbers, we find that the thermodynamic probability associated with a definite macrostate is

$$W = \sum W\{\nu_i\}. \tag{12.3}$$

As described above, the sum extends over all sets of occupation numbers $\{\nu_i\}$ for which

$$\sum_i \nu_i = \mathcal{N} \tag{12.4}$$

and

$$\sum_i \nu_i \varepsilon_i = \mathcal{E} \tag{12.5}$$

where $\mathcal{E}$ is the total energy of the system. Ideally we should evaluate the sum (12.3), but this turns out to be algebraically quite difficult. However for large $\mathcal{N}$ it is possible to obtain the same results as are given by a rigorous analysis (**F1**) based on (12.3) by means of the following approximation: we assume that there is a single term in the sum, $W_{\max}$, which dominates over all others, and we then analyze only this one partitioning of particles. We shall see below that this assumption is actually justified. For expository simplicity in what follows we shall refer to $W_{\max}$ simply as W.

From (12.2) we have

$$\ln W = \sum_i (\nu_i \ln g_i - \ln \nu_i!) \approx \sum_i [\nu_i - \nu_i \ln (\nu_i/g_i)]$$

$$= \mathcal{N} - \sum_i \nu_i \ln (\nu_i/g_i), \tag{12.6}$$

where we have made use of the dominant terms in *Stirling's formula*

$$\ln x! \approx \tfrac{1}{2} \ln 2\pi + \tfrac{1}{2} \ln x + x \ln x - x, \tag{12.7}$$

which is valid for $x \gg 1$, and we also have used the constraint (12.4). We now assume that as the system evolves, the ν_i vary as a result of collisional shuffling of particles, and approach a distribution for which W is maximum. Once this state is attained, the first variation δW resulting from small fluctuations $\delta\nu_i$ in individual occupation numbers will be zero. Thus when W has its maximum value

$$\delta W = \delta\mathcal{N} - \sum_i \delta\nu_i - \sum_i \delta\nu_i \ln (\nu_i/g_i) = -\sum_i \delta\nu_i \ln (\nu_i/g_i) = 0, \quad (12.8)$$

where we have noted from (12.4) that

$$\delta\mathcal{N} = \sum_i \delta\nu_i = 0. \tag{12.9}$$

The variations $\delta\nu_i$ cannot be arbitrary, but must satisfy both (12.9) and the

constraint, implied by (12.5), that

$$\delta \mathscr{E} = \sum_i \varepsilon_i \, \delta \nu_i = 0. \tag{12.10}$$

The standard method for solving a variational problem subject to constraints is to use the *method of Lagrange multipliers* [see, e.g., (**M2,** Appendix VI)] in which one considers the variation of a linear combination (with as-yet-undetermined coefficients) of the original equation and the constraint equations. That is, in the equation

$$\sum_i \delta \nu_i [\ln (\nu_i/g_i) - \ln \alpha + \beta \varepsilon_i] = 0 \tag{12.11}$$

we can now consider the $\delta \nu_i$'s to be, in effect, independent; the form of the coefficients in (12.11) is chosen for later convenience. The only solution of (12.11) for arbitrary $\delta \nu_i$ is

$$\nu_i = \alpha g_i e^{-\beta \varepsilon_i}, \tag{12.12}$$

and this is the distribution of occupation numbers that maximizes W.
Summing (12.12) over all i we obtain

$$\mathscr{N} = \alpha \sum_i g_i e^{-\beta \varepsilon_i} = \alpha Z \tag{12.13}$$

where

$$Z \equiv \sum_i g_i e^{-\beta \varepsilon_i} \tag{12.14}$$

is the *partition function* associated with the distribution. Combining (12.12) to (12.14) we thus have

$$(\nu_i/\mathscr{N}) = (g_i e^{-\beta \varepsilon_i})/Z \tag{12.15}$$

and hence from (12.5)

$$\mathscr{E} = (\mathscr{N}/Z) \sum_i \varepsilon_i g_i^{-\beta \varepsilon_i}. \tag{12.16}$$

Using (12.15) and (12.16) in (12.6) we find

$$\ln W = \mathscr{N}[1 + \ln (Z/\mathscr{N})] + \beta \mathscr{E} \tag{12.17}$$

whence

$$S = \mathscr{N}k[1 + \ln (Z/\mathscr{N})] + \beta k \mathscr{E}. \tag{12.18}$$

If we write $dS = (\partial S/\partial \mathscr{E})_v \, d\mathscr{E} + (\partial S/\partial V)_{\mathscr{E}} \, dV$, then we see from the first law of thermodynamics that

$$(\partial S/\partial \mathscr{E})_v = 1/T. \tag{12.19}$$

Now differentiating (12.18) with respect to $\mathscr{E}$ we find

$$(\partial S/\partial \mathscr{E})_v = k[\mathscr{E} + (\mathscr{N}/Z)(\partial Z/\partial \beta)](\partial \beta/\partial \mathscr{E}) + \beta k. \tag{12.20}$$

But from (12.14) and (12.16)

$$(\partial Z/\partial \beta) = -\sum_i \varepsilon_i g_i e^{-\beta \varepsilon_i} = -(Z/\mathcal{N})\mathscr{E}, \tag{12.21}$$

hence (12.20) reduces to

$$(\partial S/\partial \mathscr{E})_V = \beta k, \tag{12.22}$$

and therefore from (12.19) we have finally

$$\beta = 1/kT. \tag{12.23}$$

Having evaluated β we can now rewrite the above results in the usual forms

$$(\nu_i/\mathcal{N}) = (n_i/N) = [g_i \exp(-\varepsilon_i/kT)]/Z, \tag{12.24}$$

$$Z = \sum_i g_i \exp(-\varepsilon_i/kT), \tag{12.25}$$

$$\mathscr{E} = (\mathcal{N}/Z) \sum_i \varepsilon_i g_i \exp(-\varepsilon_i/kT), \tag{12.26}$$

$$S = \mathcal{N}k[1 + \ln(Z/\mathcal{N})] + (\mathscr{E}/T), \tag{12.27}$$

and

$$(\nu_m/\nu_l) = (n_m/n_l) = (g_m/g_l) \exp[-(\varepsilon_m - \varepsilon_l)/kT]. \tag{12.28}$$

Equation (12.28) is known as the *Boltzmann excitation formula*. In (12.24) and (12.28) the quantities n and N denote, as before, particle *densities* per cm³.

FLUCTUATIONS AROUND EQUILIBRIUM

Having determined the equilibrium distribution function, we are now in a position to study fluctuations around equilibrium. First, let us calculate the probability of any other distribution of occupation numbers relative to the probability of the equilibrium state. Let $\nu_i = \nu_i^0 + \Delta \nu_i$ where ν_i^0 denotes the equilibrium populations given by (12.24), and where the $\Delta \nu_i$ are fluctuations subject to the constraint (12.9). For simplicity we consider each elementary state separately, that is, $g_i \equiv 1$. Assuming $|\Delta \nu_i/\nu_i^0| \ll 1$, we have, from (12.6),

$$\ln W = \mathcal{N} - \sum_i (\nu_i^0 + \Delta \nu_i) \ln(\nu_i^0 + \Delta \nu_i)$$

$$\approx \mathcal{N} - \sum_i (\nu_i^0 + \Delta \nu_i)[\ln \nu_i^0 + (\Delta \nu_i/\nu_i^0) - \tfrac{1}{2}(\Delta \nu_i/\nu_i^0)^2] \tag{12.29}$$

$$= \ln W^0 - \tfrac{1}{2} \sum_i (\Delta \nu_i)^2/\nu_i^0 - \sum_i \Delta \nu_i - \sum_i \Delta \nu_i \ln \nu_i^0.$$

The last two terms are zero by virtue of (12.8) and (12.9), so we find

$$\ln(W/W^0) \approx -\tfrac{1}{2} \sum_i (\Delta \nu_i)^2/\nu_i^0 \tag{12.30}$$

which explicitly shows that the extremum W^0 is in fact a maximum.

Furthermore, the maximum is very sharp. To illustrate, consider a volume of $1\,\mathrm{cm}^3$ containing $\mathcal{N} = 10^{16}$ particles, and take a very small fluctuation, say $|\Delta \nu_i|/\nu_i^0 = 10^{-6}$ for all i. Then $\ln(W/W^0) = -5 \times 10^3$, or $W/W_0 \approx 10^{-2000}$, which is a very small number indeed! Thus even an extremely small departure from the equilibrium distribution implies an enormous reduction in the thermodynamic probability, and this implies that we will almost never observe a state that differs even slightly from the equilibrium state (unless, of course, the system is *driven* to that non-equilibrium state).

Next, let us inquire how large the fluctuations in the total energy of a system are likely to be. Consider a sequence of microstates $\{\nu_i^{(\lambda)}\}$, each of which satisfies (12.4) and (12.5). Let W_0 be the thermodynamic probability of the corresponding macrostate; from Boltzmann's relation $W_0 = \exp(S/k)$, therefore for any one of these microstates

$$\exp\left[(S/k) - \beta\mathscr{E}\right] = W_0 \exp\left[-\beta \sum_i \nu_i^{(\lambda)} \varepsilon_i\right] = \sum_\lambda \exp\left[-\beta \sum_i \nu_i^{(\lambda)} \varepsilon_i\right]$$

(12.31)

where the last equality takes advantage of the fact that all microstates have the same energy $\mathscr{E}$. Rewrite (12.31) as

$$W = \exp(S/k) = \sum_\lambda \exp\left[-\beta \sum_i \nu_i^{(\lambda)} \varepsilon_i + \beta\mathscr{E}\right] = \sum_\lambda \exp\left[-\beta(H_\lambda - \mathscr{E})\right].$$

(12.32)

Now relax the requirement (12.5) and suppose that the energy H_α of the αth microstate differs slightly from $\mathscr{E}$. Interpreting the right-hand side of (12.32) as the sum of probabilities contributed to the total by the individual microstates λ, we conclude that the probability that the system has a total energy H_λ is proportional to $\exp(-\beta H_\lambda)$. We therefore can calculate the average energy of a group of macrostates with energies clustered around $\mathscr{E}$ as

$$\mathscr{E} = \langle H \rangle \equiv \sum_\lambda H_\lambda e^{-\beta H_\lambda} \Big/ \sum_\lambda e^{-\beta H_\lambda}.$$

(12.33)

Differentiating (12.33) with respect to β we find

$$\frac{\partial \mathscr{E}}{\partial \beta} = \frac{\left(\sum_\lambda H_\lambda e^{-\beta H_\lambda}\right)^2}{\left(\sum_\lambda e^{-\beta H_\lambda}\right)^2} - \frac{\sum_\lambda H_\lambda^2 e^{-\beta H_\lambda}}{\sum_\lambda e^{-\beta H_\lambda}} = \mathscr{E}^2 - \langle H^2 \rangle.$$

(12.34)

Now

$$\langle H^2 \rangle = \langle (\mathscr{E} + \Delta\mathscr{E})^2 \rangle = \mathscr{E}^2 + 2\mathscr{E}\langle \Delta\mathscr{E} \rangle + \langle (\Delta\mathscr{E})^2 \rangle = \mathscr{E}^2 + \langle (\Delta\mathscr{E})^2 \rangle$$

(12.35)

where we noted that $\langle \Delta\mathscr{E} \rangle = 0$ because $\langle H \rangle = \mathscr{E}$. Combining (12.34) and (12.35) we have

$$\langle (\Delta\mathscr{E})^2 \rangle = -(\partial\mathscr{E}/\partial\beta) = kT^2(\partial\mathscr{E}/\partial T) = kT^2 C_v, \qquad (12.36)$$

where C_v is the heat capacity at constant volume. But $\mathscr{E} \propto \mathcal{N}$ and $C_v \propto \mathcal{N}$, hence

$$\langle (\Delta\mathscr{E})^2 \rangle^{1/2}/\mathscr{E} \propto \mathcal{N}^{-1/2}. \qquad (12.37)$$

Thus as $\mathcal{N} \to \infty$, almost all realizations of the physical system will have an energy very nearly equal to $\mathscr{E}$. In fact it can be shown (**H2**, 159–160) that the distribution in energy around $\mathscr{E}$ is a Gaussian with a halfwidth

$$(\Delta\mathscr{E})_{1/2} = (2kT^2 C_v)^{1/2}. \qquad (12.38)$$

Again $(\Delta\mathscr{E})_{1/2}/\mathscr{E} \propto \mathcal{N}^{-1/2}$, so as $\mathcal{N} \to \infty$, the distribution function approaches a δ-function centered on $\mathscr{E}$.

Finally, we return to the argument advanced earlier that we can replace the sum in (12.3) by a single term W_{max}. It can be shown rigorously that ln W as defined by (12.3) can differ from ln W_{max} only by terms of order ln $\mathcal{N}$ [see e.g., (**C1**, 370–375), (**D1**, 302–308), (**H2**, §7.2), or (**W1**, 90–94)]. But ln $W_{max} \propto \mathcal{N}$, hence

$$\ln (W/W_{max}) = 1 + O[(\ln \mathcal{N})/\mathcal{N}], \qquad (12.39)$$

which shows that as $\mathcal{N} \to \infty$, W_{max} provides an extremely good estimate of W.

RELATION TO THERMODYNAMICS

We can derive all thermodynamic properties of a gas from the distribution function (12.24). A particularly compact set of formulae can be obtained in terms of the partition function. Thus using (12.25) and (12.26) we have

$$\mathscr{E} = \mathcal{N}kT^2(\partial \ln Z/\partial T)_v. \qquad (12.40)$$

Therefore (12.27) can be rewritten as

$$S = \mathcal{N}k[1 + \ln (Z/\mathcal{N}) + T (\partial \ln Z/\partial T)_v], \qquad (12.41a)$$

whence

$$s = R [1 + \ln (Z/\mathcal{N}) + T (\partial \ln Z/\partial T)_v]. \qquad (12.41b)$$

Furthermore, by expanding dS and $d\mathscr{E}$ in the first law of thermodynamics in terms of dT and dV, one easily finds that

$$p = T(\partial S/\partial V)_T - (\partial\mathscr{E}/\partial V)_T \qquad (12.42)$$

and hence, from (12.40) and (12.41a),

$$p = \mathcal{N}kT (\partial \ln Z/\partial V)_T. \qquad (12.43)$$

And so on for other macroscopic variables. Thus once we know $Z(T, V)$ we can derive explicit expressions for all state variables.

THERMODYNAMIC PROPERTIES OF A PERFECT GAS

To illustrate the results derived above, let us consider a gas of $\mathcal{N}$ structureless point particles in equilibrium in a volume V. The only energy associated with such particles is their translational kinetic energy $\varepsilon = \frac{1}{2}mu^2$. Consider those particles within the phase-space volume element $dV\,d^3u = dx\,dy\,dz\,du_x\,du_y\,du_z$ centered on a position $\mathbf{x}$ and velocity $\mathbf{u}$. The distribution function f for these particles can be derived from (12.24) if we identify ν_i with $d^6\mathcal{N} = f\,dV\,d^3u$, the number of particles in the phase-space element; write $\varepsilon_i = \frac{1}{2}mu^2$; and accept from quantum statistics the *Pauli exclusion principle*, which implies that the number of states available within the phase-space element is

$$g_i = (m/h)^3\,dx\,dy\,dz\,du_x\,du_y\,du_z = (4\pi m^3/h^3)\,dx\,dy\,dz\,u^2\,du. \quad (12.44)$$

Thus

$$d^6\mathcal{N} = (4\pi m^3\mathcal{N}/h^3 Z)\exp\,(-mu^2/2kT)\,dx\,dy\,dz\,u^2\,du. \quad (12.45)$$

Integrating over V we have the velocity distribution function

$$d^3\mathcal{N} = (4\pi m^3\mathcal{N}V/h^3 Z)\exp\,(-mu^2/2kT)u^2\,du. \quad (12.46)$$

Integrating over all velocities we have

$$\mathcal{N} = (m^3\mathcal{N}V/h^3 Z)(2\pi kT/m)^{3/2}, \quad (12.47)$$

whence we obtain the partition function for translational motion

$$Z_{\text{trans}} = (2\pi mkT/h^2)^{3/2}\,V. \quad (12.48)$$

Using (12.48) in (12.45) we see that the distribution function is none other than the Maxwellian distribution

$$f(u)\,d^3u\,dV = N(m/2\pi kT)^{3/2}\exp\,(-mu^2/2kT)\,d^3u\,dV \quad (12.49)$$

as expected; here $N \equiv \mathcal{N}/V$ is the particle density per cm^3.

Given the partition function (12.48) we can calculate all the thermodynamic properties of the gas. Thus from (12.43)

$$p = \mathcal{N}kT/V = NkT, \quad (12.50)$$

which is identical to (1.2). Similarly, using (12.40), we have

$$\mathscr{E}_{\text{trans}} = \tfrac{3}{2}\mathcal{N}kT = (\tfrac{3}{2}NkT)V \quad (12.51)$$

or

$$e_{\text{trans}} = \tfrac{3}{2}RT, \quad (12.52)$$

in complete agreement with the results of kinetic theory. Then from (2.11) we recover $c_v = \tfrac{3}{2}R$, and from (4.5) $c_p = \tfrac{5}{2}R$, hence $\gamma = \tfrac{5}{3}$, again in agreement with kinetic theory. Finally, from (12.48) and (12.41), we have

$$S_{\text{trans}} = \mathcal{N}k[\tfrac{5}{2} + \ln\,(V/\mathcal{N}) + \ln\,(2\pi mkT/h^2)^{3/2}], \quad (12.53)$$

which is the *Sackur–Tetrode equation* for the entropy of translational

motions. Dividing (12.53) by $\mathcal{N}m$ and using the perfect gas law we find for the specific entropy

$$s_{\text{trans}} = \tfrac{5}{2}R \ln T - R \ln p + R[\tfrac{5}{2} + \tfrac{3}{2}\ln(2\pi m/h^2) + \tfrac{5}{2}\ln k]. \quad (12.54)$$

Comparing (12.54) with (8.23) and (4.11) we see that none of the coefficients in the equation were determined by thermodynamics; with kinetic theory we can evaluate explicitly only the coefficients of $\ln T$ and $\ln p$; but with statistical mechanics we obtain explicit results for all coefficients including the additive constant.

THERMODYNAMIC PROPERTIES OF A GAS WITH INTERNAL STRUCTURE

Consider now a gas composed of atoms that have a sequence of bound eigenstates with statistical weights g_i, lying at energies ε_i above the ground state, to which the atom's electrons can be excited. Let ε'_j be the translational energy of an atom whose velocity lies within phase-space cell j, which has statistical weight g'_j. Then the total energy of an atom excited to state i and moving in phase-space cell j is $\varepsilon = \varepsilon_i + \varepsilon'_j$, the combined statistical weight associated with this condition is $g = g_i g'_j$, and the partition function is

$$Z = \sum_i \sum_j g_i g'_j \exp\left[-(\varepsilon_i + \varepsilon'_j)/kT\right]. \quad (12.55)$$

But the distributions over translational and internal states are statistically independent of each other because atoms in a particular excited state can move at any velocity, and indeed in equilibrium must necessarily have the same Maxwellian velocity distribution as atoms in all other excitation states. For each term in the sum over i there will therefore be a complete sum over j, hence

$$Z = \sum_j g'_j e^{-\varepsilon'_j/kT} \sum_i g_i e^{-\varepsilon_i/kT} = Z_{\text{trans}} Z_{\text{elec}}. \quad (12.56)$$

Thus the partition function can be factorized.

For dilute gases, the independence of translational and internal energies is essentially perfect, and the factorization (12.56) is quite accurate. If the particles in the gas are molecules instead of atoms then there are additional energy states produced by molecular vibration and rotation, and the complete partition function becomes $Z = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} Z_{\text{elec}}$. In this case the factorization is not as accurate, however, because rapid rotation of a molecule distorts its shape and changes its vibrational potential well, while vibration changes a molecule's moments of inertia and hence affects its rotation; thus vibrational and rotational modes are explicitly coupled, contrary to the assumption used to derive (12.56). We do not consider molecules further in what follows.

The translational part of (12.56) is again given by (12.48), while the

electronic excitation part is

$$Z_{\text{elec}} = \sum_i g_i e^{-\varepsilon_{i0}/kT} \tag{12.57}$$

where the subscript zero indicates that ε is measured relative to the ground state. Formally this sum extends over an infinite number of eigenstates, and because ε approaches a limiting value ε_{I0}, the ionization potential, the individual terms remain finite and therefore (12.57) diverges. This divergence is unphysical, however, because for very large quantum numbers the eigenstates fill so large a volume that they overlap adjacent atoms in the gas; these states are so strongly perturbed that they are effectively destroyed. The sum in (12.57) can therefore be truncated after a finite number of terms [cf. (**M5**, 111 and 295)].

Because Z_{elec} is independent of V it contributes nothing to $(\partial \ln Z/\partial V)_T$, hence application of (12.43) again yields the perfect gas law. The pressure in a gas is thus independent of its internal excitation, and reflects only "external" translational motion, as would be expected from its basic definition in terms of rate of momentum transport per unit area (cf. §30). Using (12.40) to calculate the internal energy we have

$$\begin{aligned}
\mathscr{E} &= \tfrac{3}{2}\mathscr{N}kT + (\mathscr{N}/Z_{\text{elec}}) \sum_i \varepsilon_{i0} g_i e^{-\beta \varepsilon_{i0}} \\
&= \tfrac{3}{2}\mathscr{N}kT + \sum_i \nu_i \varepsilon_{i0} = \mathscr{E}_{\text{trans}} + \mathscr{E}_{\text{elec}},
\end{aligned} \tag{12.58}$$

where in the second term ν_i denotes the total number of atoms in eigenstate i without regard to velocity, and, as before, $\beta = 1/kT$. The internal energy per particle is

$$\bar{e} = \tfrac{3}{2}kT + \langle \varepsilon_{i0} \rangle, \tag{12.59}$$

where $\langle \varepsilon_{i0} \rangle \equiv \sum (\nu_i/\mathscr{N}) \varepsilon_{i0}$; per gram $e = \bar{e}/m$ where m is the mass per particle.

From (12.59) we immediately find the specific heat at constant volume:

$$c_v = \tfrac{3}{2}R + R\beta^2(\langle \varepsilon_{i0}^2 \rangle - \langle \varepsilon_{i0} \rangle^2). \tag{12.60}$$

For example, suppose the atom has only a ground state and one excited state; (12.60) then becomes

$$c_v = \tfrac{3}{2}R + R[G(\beta \varepsilon_{10})^2 e^{-\beta \varepsilon_{10}}/(1 + Ge^{-\beta \varepsilon_{10}})^2] = (c_v)_{\text{trans}} + (c_v)_{\text{elec}}, \tag{12.61}$$

where $G \equiv (g_1/g_0)$. Notice that c_v now varies and depends explicitly on T. One sees that $(c_v)_{\text{elec}}$ vanishes both as $T \to 0$ $(\beta \to \infty)$ and as $T \to \infty$ $(\beta \to 0)$, that is, when the gas is unexcited or when the excitation has "saturated" so that $(\nu_i/\nu_0) = (n_1/n_0) = (g_1/g_0)$; in both these limits heat added to the system goes directly into translational motions, and c_v reduces to the value appropriate to a gas composed of structureless particles.

Calculations using (12.61) show that c_v has a strong maximum (whose amplitude depends on the ratio G) at the temperature at which the gas first becomes appreciably excited, typically near $\beta\varepsilon_{10} \sim 2$; for $G = 1$, $(c_v)_{elec}$ reaches a maximum of about $0.45R$. Of course, the behavior of c_v for a real gas having several excitation states is more complex and in general must be computed numerically.

Because the pressure, as we saw above, is the same as for a gas of structureless particles, (2.34) again leads to $c_p = c_v + R$ where c_v is now given by (12.61). Clearly c_p is also a function of temperature, and the ratio $\gamma \equiv (c_p/c_v)$ is not constant. In this case we can no longer write equations (4.13) to (4.15) but must instead develop more general relations, as discussed in §14.

Finally, for the specific entropy we have, from (12.41b),

$$s = s_{trans} + R[\ln Z_{elec} + T(\partial \ln Z_{elec}/\partial T)_v]$$

$$= s_{trans} + R\left[\ln\left(\sum_i g_i e^{-\beta\varepsilon_{i0}}\right) + (\langle\varepsilon_{i0}\rangle/kT)\right] \tag{12.62}$$

$$= s_{trans} + s_{elec},$$

where s_{trans} is given by (12.54). As was true for e and c_v, a major contribution to s comes from the internal excitation term s_{elec}.

INTERPRETATION OF THE BOLTZMANN H-THEOREM

The results of statistical mechanics afford us the means by which we can make a physical interpretation of Boltzmann's H-theorem. Again consider an isolated, homogeneous sample of a gas composed of structureless particles, with no external forces applied. An expression for the entropy in terms of the distribution function f can be derived directly from (12.6) by (1) writing $\nu_i = f(u_i)\,d^3u\,dV$, (2) using (12.44) for g_i, and (3) replacing the sum by integrations over $d^3u\,dV$. We find

$$S = k \ln W = k\mathcal{N} - kV\int \ln (h^3 f/m^3) f\,d^3u. \tag{12.63}$$

Differentiating (12.63) with respect to time, and recognizing that $(\partial f/\partial t)$ under the restrictions stated above is $(Df/Dt)_{coll}$, we obtain

$$(dS/dt) = -kV\int [1 + \ln (h^3 f/m^3)](Df/Dt)_{coll}\,d^3u$$

$$= -kV\int\int\int [1 + \ln (h^3 f/m^3)](f_1'f_2' - f_1 f_2)g\sigma(\Omega)\,d\Omega\,d^3u_1\,d^3u_2. \tag{12.64}$$

and hence that $(dS/dt) \geq 0$, the equality holding in equilibrium. Thus the physical content of Boltzmann's H-theorem is that the entropy of an isolated system continually increases to its equilibrium value (at which

point the distribution function is Maxwellian), in agreement with the conclusions reached in §3 from thermodynamic considerations.

13. Ionization

In the process of *ionization* a bound electron is removed from one of the discrete eigenstates of an atom into a *continuum* of levels in which it is unbound and has a finite kinetic energy at infinite distance from the atom whence it came. This continuum begins at an energy ε_{I0}, the ionization potential of the atom above the ground state. Every species of atom has a sequence of ionization stages, each with a progressively higher ionization potential as successive electrons are removed, leading ultimately to a completely stripped nucleus. The relative number of atoms and ions in successive ionization stages can be computed using the *Saha ionization formula*, which can be derived as an extension of the Boltzmann excitation formula to the continuum.

Consider a process in which an atom in its ground level is ionized, yielding an ion in its ground level plus a free electron moving with speed u in the continuum. The total energy of the final state of the system relative to its initial state is $\varepsilon = \varepsilon_{I0} + \frac{1}{2}mu^2$ where m is the mass of an electron. Let the statistical weight of the atom be $g_{0,0}$ and of the ion $g_{0,1}$ where the first subscript denotes the atomic level (in this case the ground level) and the second indicates the ionization stage. Using (12.44) we assign a statistical weight

$$g_{\text{electron}} = 2(m/h)^3 \, dV(4\pi u^2) \, du \tag{13.1}$$

to an electron in a volume element dV moving with a speed on the range $(u, u+du)$; the factor of 2 has a quantum-mechanical origin and accounts for the two possible *spin* states of the free electron. The statistical weight of the combined electron + ion system is $g = g_{0,1}g_{\text{electron}}$.

Integrate over a volume element large enough to contain exactly one electron (i.e., we consider a unit process), so that we can replace dV by $(1/n_e)$ where n_e is the number density of free electrons. We can then apply (12.28) to the final system with electrons having velocities $(u, u+du)$ to obtain

$$[n_{0,1}(u)/n_{0,0}] = 8\pi(m/h)^3(g_{0,1}/g_{0,0})(1/n_e) \exp\left[-(\varepsilon_{I0}+\tfrac{1}{2}mu^2)/kT\right]u^2 \, du. \tag{13.2}$$

Then summing over all possible final states by integrating over all electron velocities we have

$$(n_{0,1}/n_{0,0}) = (8\pi m^3 g_{0,1}/h^3 g_{0,0}n_e)(2kT/m)^{3/2}e^{-\varepsilon_{I0}/kT}\int_0^\infty x^2 e^{-x^2} \, dx. \tag{13.3}$$

Or, evaluating the integral,

$$n_{0,0} = n_{0,1}n_e\tfrac{1}{2}(h^2/2\pi mkT)^{3/2}(g_{0,1}/g_{0,0}) \exp(\varepsilon_{I0}/kT). \tag{13.4}$$

Notice that in (13.2) to (13.4), and in the equations that follow, the n's are particle *densities* (per cm^3).

In the above derivation, no essential use is made of information about which initial ionization stage is being considered, and (13.4) can actually be applied to any two successive stages $(j, j + 1)$, yielding

$$n_{0,j} = n_{0,j+1} n_e \tfrac{1}{2} (h^2/2\pi m k T)^{3/2} (g_{0,j}/g_{0,j+1}) \exp{(\varepsilon_{Ij}/kT)}. \tag{13.5}$$

By using (12.28) in (13.5) we can obtain the occupation number of any excitation level of ion j in terms of the temperature, electron density, and the ground-state population of ion $(j + 1)$:

$$\begin{aligned}
n_{i,j} &= C_I n_{0,j+1} n_e (g_{i,j}/g_{0,j+1}) T^{-3/2} \exp{[(\varepsilon_{Ij} - \varepsilon_{ij})/kT]} \\
&\equiv n_{0,j+1} n_e \Phi_{ij}(T).
\end{aligned} \tag{13.6}$$

In (13.6), ε_{ij} is the energy of excitation state i of ion j relative to that ion's ground state (hence $\varepsilon_{Ij} - \varepsilon_{ij}$ is the ionization potential from level i of ion state j to the ground state of ion $j + 1$), and the numerical constant is $C_I = 2.07 \times 10^{-16}$ in cgs units. This is perhaps the most useful form of Saha's equation for our later work; it is sometimes called the *Saha–Boltzmann formula*.

Using (12.24) in (13.6) for ionization stage $j + 1$ we find

$$n_{i,j} = N_{j+1} n_e (g_{ij}/Z_{j+1}) \Phi_{ij}(T), \tag{13.7}$$

and again, for ionization stage j, we have

$$N_j = C_I N_{j+1} n_e (Z_j/Z_{j+1}) T^{-3/2} \exp{(\varepsilon_{Ij}/kT)} \equiv N_{j+1} n_e \Phi_j(T). \tag{13.8}$$

Equation (13.8) gives the relation between the total densities of atoms in the two ionization stages, irrespective of their excitation states.

In practically all of our later work we shall restrict attention to pure hydrogen for which only one ionization transition is possible. For hydrogen, the statistical weight of quantum level i is $g_i = 2i^2$, and the statistical weight of the ion is $g_p = 1$. The energy of level i below the continuum is ε_H/i^2 where ε_H equals one rydberg (13.6 eV). Thus (13.6) becomes

$$n_i = 2C_I i^2 n_e n_p T^{-3/2} \exp{(\varepsilon_H/i^2 kT)} \equiv n_e n_p \Phi_{iH}(T). \tag{13.9}$$

Similarly (13.8) becomes

$$n_H = C_I n_e n_p Z_H T^{-3/2} \exp{(\varepsilon_H/kT)} \equiv n_e n_p \Phi_H(T) \tag{13.10}$$

where

$$Z_H \equiv \sum_{i=1} 2i^2 \exp{(-\varepsilon_{iH}/kT)}. \tag{13.11}$$

Here

$$\varepsilon_{iH} \equiv (1 - i^{-2}) \varepsilon_H. \tag{13.12}$$

14. Thermodynamic Properties of Ionizing Hydrogen

Let us now examine the effects of ionization on the thermodynamic properties of a gas. We restrict attention to pure hydrogen, and thereby account for the dominant process in astrophysical plasmas with only a minimum of complication. The density of a pure hydrogen gas is

$$\rho = n_H m_H + n_p m_p + n_e m_e. \tag{14.1}$$

But, by charge conservation,

$$n_e = n_p, \tag{14.2}$$

hence

$$\rho = n_H m_H + n_p(m_p + m_e) = (n_H + n_p)m_H \equiv N_H m_H. \tag{14.3}$$

Here N_H denotes the total number density of hydrogen atoms and ions in all forms.

As was true for internal excitation (cf. §12), in an ionizing gas only the translational degrees of freedom contribute to the pressure, so

$$p = NkT \tag{14.4}$$

where now

$$N = n_H + n_p + n_e = N_H + n_e. \tag{14.5}$$

Let x denote the *degree of ionization* of the material,

$$x \equiv n_p/(n_p + n_H) = n_p/N_H. \tag{14.6}$$

In terms of the degree of ionization, Saha's formula (13.10) becomes

$$x^2/(1-x) = \text{Const. } VT^{3/2}e^{-\varepsilon_H/kT}/Z_H \tag{14.7a}$$

or, equivalently,

$$x^2 p/(1-x^2) = \text{Const. } T^{5/2}e^{-\varepsilon_H/kT}/Z_H. \tag{14.7b}$$

Furthermore, the equation of state can be written

$$p = (1+x)N_H kT = (1+x)\rho \mathcal{R} T. \tag{14.8}$$

If we regard (T, p) [or equivalently (T, N)] as given, then using (13.10) in (14.5) we obtain a quadratic for n_e:

$$n_e^2 \Phi_H + 2n_e = N, \tag{14.9}$$

which yields

$$n_e = [(N\Phi_H + 1)^{1/2} - 1]/\Phi_H. \tag{14.10}$$

Once we know n_e we can compute all the n_i immediately from (13.9).

The specific internal energy is simply the sum of the translational,

excitation, and ionization energies of the particles per gram of material:

$$e = \left[\tfrac{3}{2}(N_H + n_e)kT + \sum_i n_i \varepsilon_{iH} + n_p \varepsilon_H\right]\bigg/ N_H m_H$$

$$= \tfrac{3}{2}(1+x)\mathfrak{R}T + \left[(1-x)\sum_i (n_i/n_H)\varepsilon_{iH} + x\varepsilon_H\right]\bigg/ m_H \qquad (14.11a)$$

$$= \tfrac{3}{2}(1+x)\mathfrak{R}T + [(1-x)\langle\varepsilon_{iH}\rangle + x\varepsilon_H]/m_H$$

or per heavy particle (i.e., atom or proton), which is more convenient in what follows,

$$\bar{e} = \tfrac{3}{2}(1+x)kT + (1-x)\langle\varepsilon_{iH}\rangle + x\varepsilon_H. \qquad (14.11b)$$

Equation (14.11) was written directly from its physical meaning; it can of course also be derived from (12.40) if Z_{elec} is extended to include ionization. The specific enthalpy per particle follows immediately from (14.4) and (14.11b):

$$\bar{h} = \tfrac{5}{2}(1+x)kT + (1-x)\langle\varepsilon_{iH}\rangle + x\varepsilon_H. \qquad (14.12)$$

Computations with the Saha equation show that hydrogen in stellar ionization zones is strongly ionized even when $\varepsilon_H/kT \sim 10$; thus the ionization term $x\varepsilon_H$ makes a very large contribution to $\bar{e}$, and represents a large energy reservoir in the material.

In practice, because the first excited state of hydrogen lies at an energy of $\tfrac{3}{4}\varepsilon_H$ above ground, one finds from the Boltzmann and Saha formulae that whenever hydrogen has even a small population in any excited state, it is already strongly ionized and therefore $(1-x) \ll 1$. Hence in (14.11) and (14.12) it is a good approximation simply to neglect the term in $\langle\varepsilon_{iH}\rangle$, which we drop henceforth. It is also for this reason that we can set $Z_H = g_{0,0}$ and ignore the temperature dependence of the partition function in (14.7).

With these simplifications it is now relatively easy to calculate the specific heats of ionizing hydrogen. Thus the specific heat at constant volume, per heavy particle, is

$$\bar{c}_v = c_v m_H = (\partial\bar{e}/\partial T)_v = \tfrac{3}{2}k(1+x) + (\tfrac{3}{2}kT + \varepsilon_H)(\partial x/\partial T)_v. \qquad (14.13)$$

Differentiating (14.7a) logarithmically, we obtain

$$\frac{1}{x}\left(\frac{2-x}{1-x}\right)\left(\frac{\partial x}{\partial T}\right)_v = \frac{1}{T}\left(\frac{3}{2} + \frac{\varepsilon_H}{kT}\right), \qquad (14.14)$$

whence

$$(\bar{c}_v/k) = (c_v/\mathfrak{R}) = \tfrac{3}{2}(1+x) + \frac{x(1-x)}{(2-x)}\left(\frac{3}{2} + \frac{\varepsilon_H}{kT}\right)^2. \qquad (14.15)$$

Clearly, as $x \to 0$ or $x \to 1$, $\bar{c}_v$ reduces to the contribution from translational energy only; when the material is partially ionized (e.g., when

$x \approx \frac{1}{2}$), $\tilde{c}_v$ can greatly exceed this value. This large increase reflects the fact that when the gas is ionizing, a large fraction of the heat input to the gas is consumed in further ionizing the material rather than in raising its temperature.

Similarly, the specific heat at constant pressure per heavy particle is

$$\tilde{c}_p = (\partial \bar{h}/\partial T)_p = \frac{5}{2}k(1+x) + (\frac{5}{2}kT + \varepsilon_H)(\partial x/\partial T)_p. \qquad (14.16)$$

Differentiating (14.7b) logarithmically, we obtain

$$(\partial x/\partial T)_p = \frac{1}{2}x(1-x^2)[\frac{5}{2} + (\varepsilon_H/kT)]/T, \qquad (14.17)$$

whence

$$(\tilde{c}_p/k) = (c_p/\mathcal{R}) = \frac{5}{2}(1+x) + \frac{1}{2}x(1-x^2)[\frac{5}{2} + (\varepsilon_H/kT)]^2. \qquad (14.18)$$

Again, $\tilde{c}_p$ approaches its pure translational value as $x \to 0$ or $x \to 1$ and is much larger than that value for partially ionized material.

From the results obtained above, it is obvious that the ratio $\gamma \equiv (c_p/c_v)$ is no longer a constant, hence for adiabatic changes we cannot recover relations (4.13) to (4.15). But, following Chandrasekhar (**C1**, 121), it is natural to introduce the *generalized adiabatic exponents* $\Gamma_1, \Gamma_2, \Gamma_3$, defined to be those values for which

$$(dp/p) - \Gamma_1(d\rho/\rho) = 0, \qquad (14.19)$$

$$(dp/p) - [\Gamma_2/(\Gamma_2 - 1)](dT/T) = 0, \qquad (14.20)$$

and

$$(dT/T) - (\Gamma_3 - 1)(d\rho/\rho) = 0 \qquad (14.21)$$

for adiabatic processes in an ionizing gas. Clearly these gammas are variable (functions of T, x, etc.). It is obvious that only two of the gammas are independent, and that one has a general identity

$$\Gamma_1/(\Gamma_3 - 1) \equiv \Gamma_2/(\Gamma_2 - 1). \qquad (14.22)$$

For an adiabatic change, we know from (2.3) that

$$de = (p/\rho^2) \, d\rho, \qquad (14.23)$$

and from (14.8) we have

$$(dp/p) = [dx/(1+x)] + (d\rho/\rho) + (dT/T). \qquad (14.24)$$

Also, from (14.11a),

$$de = \frac{3}{2}(1+x)\mathcal{R} \, dT + [\frac{3}{2}\mathcal{R}T + (\varepsilon_H/m_H)] \, dx. \qquad (14.25)$$

Thus, using (14.25) in (14.23), and eliminating $(d\rho/\rho)$ via (14.24), we find

$$\frac{dp}{p} = \frac{5}{2}\frac{dT}{T} + \left(\frac{5}{2} + \frac{\varepsilon_H}{kT}\right)\frac{dx}{1+x}. \qquad (14.26)$$

But, from (14.7b),

$$\frac{2\,dx}{x(1-x^2)} = \left(\frac{5}{2}+\frac{\varepsilon_H}{kT}\right)\frac{dT}{T}-\frac{dp}{p}.$$
(14.27)

Therefore, using (14.27) to eliminate $dx/(1+x)$ from (14.26) we find, in view of (14.20),

$$\left(\frac{\Gamma_2-1}{\Gamma_2}\right) \equiv \left(\frac{\partial \ln T}{\partial \ln p}\right)_s = \frac{2+x(1-x)[\frac{5}{2}+(\varepsilon_H/kT)]}{5+x(1-x)[\frac{5}{2}+(\varepsilon_H/kT)]^2}.$$
(14.28)

Clearly, in the limits $x \to 0$ or $x \to 1$, $(\Gamma_2-1)/\Gamma_2 \to \frac{2}{5}$, which equals $(\gamma-1)/\gamma$ for a perfect gas. When hydrogen is partially ionized, $(\Gamma_2-1)/\Gamma_2$ can become as small as 0.1.

By similar analyses it is fairly easy to show that

$$\Gamma_1 = \left(\frac{\partial \ln p}{\partial \ln \rho}\right)_s = \frac{5+x(1-x)[\frac{5}{2}+(\varepsilon_H/kT)]^2}{3+x(1-x)\{\frac{3}{2}+[\frac{3}{2}+(\varepsilon_H/kT)]^2\}},$$
(14.29)

and

$$\Gamma_3 - 1 = \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_s = \frac{2+x(1-x)[\frac{5}{2}+(\varepsilon_H/kT)]}{3+x(1-x)\{\frac{3}{2}+[\frac{3}{2}+(\varepsilon_H/kT)]^2\}},$$
(14.30)

which clearly satisfy (14.22).

In many applications it is convenient to write the equation of state as

$$p = \rho k T/\mu m_H,$$
(14.31)

where μ is the *mean molecular weight*, which may be variable and hence a function of state variables. In the present case we have, from (14.8),

$$\mu = 1/(1+x).$$
(14.32)

When one considers small-amplitude perturbations around an ambient state, the quantity

$$Q \equiv 1 - (\partial \ln \mu/\partial \ln T)_p$$
(14.33)

often appears. In the present case we can use (14.17) to evaluate Q as

$$Q = 1 + \tfrac{1}{2}x(1-x)[\tfrac{5}{2}+(\varepsilon_H/kT)].$$
(14.34)

All of the results derived in this section apply to a gas composed of a single element. Results for mixtures of ionizing gases can be found in (**C5**, §§9.13–9.18), (**K2**), (**M3**, §5.4), (**M4**), and (**U1**, §§56 and 57).

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