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CHAPTER

6

THE KINETIC THEORY OF DILUTE GASES*

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Introduction

In Chapters 6 and 7 we shall attempt to give a microscopic explanation of the macroscopic properties observed in dilute and moderately dense gases.

The macroscopic properties discussed here can be classified into: (1) *general* properties—which are to a large extent insensitive to the precise nature of the intermolecular potential field—and (2) *special* properties—which depend sensitively on the intermolecular potential field. Included in the first class are: the irreversible approach to thermal equilibrium of a gas which initially is not in thermal equilibrium and the validity of the hydrodynamical equations (or the laws of irreversible thermodynamics). Included in the second class are: the temperature dependence of the thermodynamic functions and the transport coefficients of the gas.

A microscopic explanation here means an explanation based on the motion of the atoms and/or molecules which make up the gas, assuming the interatomic or intermolecular potential field is known. The determination of the intermolecular potential is, in principle, a quantum mechanical problem. We will always assume in this chapter that the intermolecular potential is additive, depends only on the intermolecular distance, and is short ranged, (i.e., it falls off rapidly to zero when the intermolecular distance exceeds a few angstroms).

The main problem we shall be concerned with will be the statistical

* See references 1-4 for general background.

problem of making the connection between the microscopic properties of the molecules, on the one hand, and the macroscopic properties of the gas in bulk, on the other hand.

The difficulty of the problem is due to the fact that matter in bulk consists of an enormous number of molecules. One cubic centimeter of air, for example, consists of $n = 3 \times 10^{19}$ molecules at a temperature of 0°C and a pressure of 1 atm. Therefore a microscopic explanation of the behavior of matter in bulk seems to involve the solution of the equations of motion of an enormous number of particles. Since the analytic solution of the equations of motion of three particles is unknown, the solution of the equations of motion for n particles seems completely hopeless.

Already in the beginning of the kinetic theory of gases in the middle of the last century, Clausius, Maxwell, and Boltzmann realized that even if one had the solution of the microscopic equations of motion for the motion of the molecules, one still would have to connect this solution with such macroscopic concepts as the local density, the local temperature, viscosity, etc. They realized that these macroscopic concepts were in some way related to averages over the microscopic behavior of the gas. Furthermore, they realized that by considering certain well-chosen averages, it might be possible to avoid the necessity of obtaining the full solution of the microscopic equations of motion of all particles because one could hope that for the determination of these averages different and much simpler equations might be used. Of course, these simplified equations would still contain *some* features of the microscopic equations of motion of the molecules but would, hopefully, be much easier to handle!

In the case of a *dilute* gas, where only binary collisions between the molecules occur, Maxwell and Boltzmann assumed that it was sufficient to consider the average number of particles, $f(\mathbf{rv}t)$, which are at time t at the position \mathbf{r} with velocity \mathbf{v} , for a description of the macroscopic properties of the gas in bulk. In this chapter we will discuss how one has been able to explain many of the observed macroscopic properties of dilute gases on the basis of this assumption. Also, we will discuss the equation which f satisfies, those microscopic averages with which the macroscopic quantities of the gas can be identified, the question of whether or not the so-defined macroscopic quantities actually do exhibit the same properties as the corresponding observed macroscopic quantities of the gas.

In the case of a *moderately dense* gas, Bogolubov conjectured that f would still be sufficient to explain the macroscopic properties of such a gas. In Chapter 7 we will see how far this conjecture is correct. This

I. The Boltzmann Equation

chapter is intended as an introduction to what has been accomplished so far. In fact, concrete results have been obtained only for the case where the intermolecular forces are purely repulsive and where only binary and ternary collisions between the molecules occur.

I. The Boltzmann Equation (5)

As we already pointed out in the introduction, Maxwell and Boltzmann realized that for an adequate description of the dilute gas one should consider $f(\mathbf{rv}t)$, the average number of particles at a given position \mathbf{r} with velocity \mathbf{v} at time t . Boltzmann was the first to write down "an equation of motion" for f , that is, an equation for the rate of change of f with time. This equation, *the Boltzmann equation*, reads in the absence of an outside field of force as:

$$\frac{\partial f(\mathbf{rv}t)}{\partial t} = -\mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} + J(ff) \quad (6.1a)$$

where

$$J(ff) = \int d\mathbf{v}_1 \int d\mathbf{b} \int d\mathbf{b}' \int d\mathbf{v}' g [f(\mathbf{rv}'t)f(\mathbf{rv}_1't) - f(\mathbf{rv}t)f(\mathbf{rv}_1't)] \quad (6.1b)$$

The meaning of the symbols in eq. (6.1a,b) will be explained below. For our purposes this equation is sufficiently general. In case there is an outside field of force, \mathbf{F} , present, one has an additional term on the right-hand side: $-(\mathbf{F}/m) \cdot (\partial f / \partial \mathbf{v})$.

We can see how eq. (6.1) is arrived at by the following elementary considerations. If one multiplies both sides of eq. (6.1) by $d\mathbf{r} d\mathbf{v}$, the left-hand side (l.h.s.) of eq. (6.1a) gives the change per unit time of the number of molecules with velocity between \mathbf{v} and $\mathbf{v} + d\mathbf{v}$ in a volume element $d\mathbf{r}$ around \mathbf{r} . In other words, the left-hand side of eq. (6.1a) then gives the rate of change of the number of molecules, $f d\mathbf{r} d\mathbf{v}$, in the volume element $d\mathbf{r} d\mathbf{v}$ around the point \mathbf{r} , \mathbf{v} in μ -space, the six-dimensional phase space of a (single) molecule,*†

According to eq. (6.1a), this rate of change is equal to the sum of a streaming term, $-\mathbf{v} \cdot (\partial f / \partial \mathbf{r}) d\mathbf{r} d\mathbf{v}$, and a collision term, $J(ff) d\mathbf{r} d\mathbf{v}$.

Of these two terms, the *streaming term* gives the rate of change of f due to the fact that the molecules have a finite velocity and, consequently,

* μ stands for "molecule."

† The volume element $d\mathbf{r} d\mathbf{v}$ in μ -space should be physically infinitesimal, i.e., it should be chosen large enough so that it contains many molecules. On the other hand, it should be small enough so that the macroscopic quantities of the gas do not change appreciably over $d\mathbf{r}$.

change their positions with time. Thus molecules with velocity \mathbf{v} around \mathbf{r} at time t will be around $\mathbf{r} + \mathbf{v} dt$ a little time dt later. While other molecules, viz., those around $\mathbf{r} - \mathbf{v} dt$, will be around \mathbf{r} at time dt .

Therefore one has for the change of $f d\mathbf{r} d\mathbf{v}$ by streaming per unit time:

loss: all molecules in $d\mathbf{r} d\mathbf{v}$ around \mathbf{r} , that is, $f(\mathbf{r}\mathbf{v}t) d\mathbf{r} d\mathbf{v}$;

gain: all molecules in $d\mathbf{r} d\mathbf{v}$ around $\mathbf{r} - \mathbf{v} dt$,
that is, $f(\mathbf{r} - \mathbf{v} dt, \mathbf{v}, t) d\mathbf{r} d\mathbf{v}$;

$$\text{balance} \quad [f(\mathbf{r} - \mathbf{v} dt, \mathbf{v}, t) - f(\mathbf{r}, \mathbf{v}, t)] d\mathbf{r} d\mathbf{v} = -\mathbf{v} \cdot \frac{\partial f(\mathbf{r}\mathbf{v}t)}{\partial \mathbf{r}} d\mathbf{r} d\mathbf{v} \quad (6.2)$$

The streaming term is therefore a "gain-loss" term.

This gain-loss character is even clearer for the *collision term*, which gives the rate of change of f due to the fact that the molecules change their velocities with time because of the forces exerted on them during collisions.

Specifically, the contribution of the last term on the right-hand side (r.h.s.) of eq. (6.1a), $-d\mathbf{r} d\mathbf{v} \int d\mathbf{v}_1 \int db b \int d\psi g f(\mathbf{r}\mathbf{v}t) f(\mathbf{r}\mathbf{v}_1t)$, gives the *loss* per unit time of the number of molecules $f d\mathbf{r} d\mathbf{v}$ with velocity \mathbf{v} around \mathbf{r} due to collisions with molecules with any velocity \mathbf{v}_1 around \mathbf{r} . In fact, any such collision between two molecules with velocities \mathbf{v} and \mathbf{v}_1 will result in two molecules with different velocities \mathbf{v}' and \mathbf{v}'_1 , respectively. Therefore any $(\mathbf{v}, \mathbf{v}_1)$ -collision results in a loss to $f d\mathbf{r} d\mathbf{v}$ because a molecule with velocity \mathbf{v}' is *not* part of $f d\mathbf{r} d\mathbf{v}$. The number of $(\mathbf{v}, \mathbf{v}_1)$ -collisions (or also *direct collisions*) per unit time can be computed by considering the relative motion of a molecule with velocity \mathbf{v} with respect to a molecule with velocity \mathbf{v}_1 .

The relative motion is characterized by the relative velocity $\mathbf{g} = \mathbf{v} - \mathbf{v}_1$, the impact parameter b and the azimuth angle ψ of the plane in which the relative motion takes place. The number of collisions in time dt of molecules with velocity \mathbf{v} with a molecule with velocity \mathbf{v}_1 , such that impact parameter b is between b and $b + db$, and the azimuth angle ψ is between ψ and $\psi + d\psi$, is given by the number of molecules with velocity \mathbf{v} in the "collision cylinder"† of volume $gb db d\psi dt$, and equals (cf. Fig. 1):

$$b db d\psi g f(\mathbf{r}\mathbf{v}t) d\mathbf{v} dt$$

where $g = |\mathbf{g}|$.

*Strictly speaking, "with velocities between \mathbf{v} and $\mathbf{v} + d\mathbf{v}$." For brevity, we will omit this more elaborate description of the set $f d\mathbf{r} d\mathbf{v}$. Similarly, "in $d\mathbf{r}$ around \mathbf{r} " will be replaced in the text simply by "around \mathbf{r} ."

†Strictly speaking, the figure is not a cylinder, but common usage often refers to it as a collision cylinder.

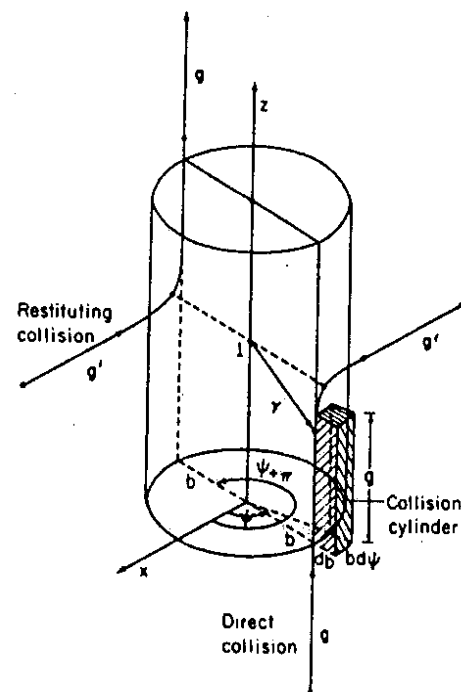


Fig. 1. Direct and restituting-collisions in relative coordinate system. [For Appendix B, Chapter 7; $\mathbf{r} \rightarrow \mathbf{r}_{21}$; $\mathbf{g} \rightarrow \mathbf{g}_{21}$; $\mathbf{g}' \rightarrow \mathbf{g}'_{21}$.]

If the gas is sufficiently dilute so that the (collision) cylinders associated with *all* molecules with velocity \mathbf{v}_1 around \mathbf{r} can be assumed not to overlap, then the total number of direct collisions per unit time around \mathbf{r} —and consequently also the *loss* of molecules with velocity \mathbf{v} around \mathbf{r} —is given by

(all molecules with velocity \mathbf{v} colliding with a molecule with velocity \mathbf{v}_1)

$$\text{loss:} \quad d\mathbf{r} d\mathbf{v} \int d\mathbf{v}_1 \int db b \int d\psi g f(\mathbf{r}\mathbf{v}t) f(\mathbf{r}\mathbf{v}_1t) \quad (6.3a)$$

(all molecules with velocity \mathbf{v}_1 in $d\mathbf{r}$ around \mathbf{r}).

The contribution of the second term on the r.h.s. of eq. (6.1a),

$$dr dv \int dv_1 \int db b \int d\psi g f(\mathbf{rv}'t) f(\mathbf{rv}_1't),$$

gives the *gain* per unit time to $f dr dv$ due to collisions. This gain can be computed in the same way as the loss to $f dr dv$ was computed before. Two molecules with velocities \mathbf{v} and \mathbf{v}_1 will result if two molecules with velocities \mathbf{v}' and \mathbf{v}'_1 (and the same impact parameter b , but with azimuth angle $\psi + \pi$) collide (compared with Fig. 1). Therefore any such $(\mathbf{v}', \mathbf{v}'_1)$ -collision will result in a gain to $f dr dv$. Using then that $|g'| = |\mathbf{v}' - \mathbf{v}'_1| = g' = g$, that $dv dv_1 = dv' dv'_1$, and assuming again that the collision cylinders associated with different molecules with velocity \mathbf{v}'_1 around dr do not overlap, one finds that the total number of $(\mathbf{v}', \mathbf{v}'_1)$ -collisions (or also *restituting collisions*) per unit time around \mathbf{r} —and consequently, also the *gain* of molecules with velocity \mathbf{v} around \mathbf{r} —is given by

$$\text{gain:} \quad dr dv \int dv_1 \int db b \int d\psi g f(\mathbf{rv}'t) f(\mathbf{rv}_1't) \quad (6.3b)$$

The balance of the gain-loss contributions leads with eqs. (6.1b), (6.3a), and (6.3b) to the following contribution to the change of $f dr dv$ per unit time:

$$\text{balance:} \quad J(ff) dr dv \quad (6.3c)$$

Equation (6.1) results from the eqs. (6.2) and (6.3c), after division by $dr dv$.

A. REMARKS ABOUT $J(ff)$

- (a) In $J(ff)$, $b db d\psi$ is the classical differential scattering cross section.
- (b) The connection between \mathbf{v} , \mathbf{v}_1 and \mathbf{v}' , \mathbf{v}'_1 (and vice versa) involves implicitly the intermolecular potential field $\phi(r)$.
- (c) The occurrence in J of two f 's indicates that only contributions from binary collisions are considered in the calculation of $\partial f / \partial t$.
- (d) The numbers of direct and restituting collisions, as given by the eqs. (6.3a) and (6.3b), respectively, are a consequence of a certain Stoszahl-Ansatz.* In fact, the numbers have been computed using a statistical assumption; the assumption of *molecular chaos*, viz: it is assumed that at every time t there are no velocity correlations at \mathbf{r} so that the average

* Stoszahl-Ansatz is an assumption about the number of collisions.

I. The Boltzmann Equation

number of molecular pairs with velocity \mathbf{v} and \mathbf{v}_1 at \mathbf{r} , $f_2(\mathbf{rvv}_1t)$, can be written as

$$f_2(\mathbf{rvv}_1t) = f(\mathbf{rv}t)f(\mathbf{rv}_1t) \quad (6.4)$$

and similarly for \mathbf{v}' and \mathbf{v}'_1 .

This statistical assumption is of a nonmechanical nature, and is the origin of the lack of time-reversal invariance of the Boltzmann equation and of the irreversible behavior shown by a gas described by the Boltzmann equation (6.1) (cf. Section II). For, changing t to $-t$, and consequently also $\mathbf{v} [= (d\mathbf{r}/dt)]$ to $-\mathbf{v}$, the l.h.s. of eq. (6.1a) and the first term on the r.h.s. of eq. (6.1a) change sign, while the second term on the r.h.s. of eq. (6.1a) [i.e., $J(ff)$] does *not*. If, therefore, $f(\mathbf{rv}t)$ is a solution of eq. (6.1) then $f(\mathbf{r}, -\mathbf{v}, -t)$ is *not*. This is in contrast to mechanics where the basic equations (for example, the Lagrange equations) are time-reversal invariant. In that case, corresponding to any solution $q(t)$ of the Lagrange equation:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) - \frac{\partial L}{\partial q} = 0 \quad (6.5a)$$

there is a solution $q(-t)$ of the time-reversed (but identical) equation:

$$\frac{d}{d(-t)} \frac{\partial L}{\partial(-\dot{q})} - \frac{\partial L}{\partial q} = 0 \quad (6.5b)$$

Thus $q(t)$ and $q(-t)$ are *both* possible solutions of the mechanical equations of motion.

It is clear that the statistical or "average" treatment of the mechanics of the molecules at \mathbf{r} is the origin of this difference with mechanics.

The approximate nature of the hypothesis of molecular chaos and, therefore, of the Stoszahl-Ansatz is reflected in the fact that the resulting Boltzmann equation (6.1) only describes the approach of a dilute gas *towards* equilibrium, but not the fluctuations *around* equilibrium when the gas is in equilibrium.

B. SUMMARY

We conclude this section by summarizing all the assumptions inherent in the Boltzmann equation:

- (1) A dilute gas can be adequately described by the single particle distribution function $f(\mathbf{rv}t)$ alone.
- (2) Only binary collisions are considered.
- (3) The molecules move according to the laws of classical mechanics.
- (4) The assumption of molecular chaos is used in the Stoszahl-Ansatz.

(5) A spherically symmetric intermolecular potential field $\phi(r)$ is assumed so that the initial velocities (v', v'_1) of the molecules in the restituting collision are equal, for all b and ψ , to the final velocities of the molecules in the direct collision, as has been used in the derivation of eq. (6.1).

(6) The number of molecules with velocities v and v_1 in the direct collision—or with velocities v' and v'_1 in the restituting collision—that are going to collide at time t has been computed as if the two colliding molecules were at the same position r , in spite of the fact that they are outside the range of the intermolecular forces.

For the existence of the Boltzmann equation it is not necessary to assume that the intermolecular potential field has a finite range, that is, that $\phi(r)$ vanishes for all $r > r_0$. One only needs to assume that $\phi(r)$ decreases sufficiently fast with increasing r so that the collision integral $J(f\bar{f})$ exists. For the existence of $J(f\bar{f})$, v and v_1 must approach v' and v'_1 sufficiently fast for increasing b .

II. Approach to Equilibrium I (H-Theorem and Principle of the Chapman-Enskog Solution)

All macroscopic properties of a dilute gas should follow from the Boltzmann equation. In this section we shall study some general questions concerning the approach to equilibrium:

(A) Can one show that a gas, which is initially (i.e., at time zero), not in equilibrium, will always approach equilibrium?

(B) Furthermore, how does this approach to equilibrium proceed?

A. H-THEOREM (6)

The general approach of a dilute gas to equilibrium could be proved by Boltzmann on the basis of his equation *without solving it for f* by the H-theorem. In fact, he proved that a dilute gas, whose time evolution is governed by the Boltzmann equation (6.1), will, for any initial state $f(\mathbf{rv}t)$, approach to thermal equilibrium which is characterized by the Maxwell distribution function $f_M(v)$,

$$f_M(v) = n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(- \frac{mv^2}{2kT} \right) \quad (6.6)$$

where m is the mass of a molecule, n is the number density, k is Boltzmann's constant, and T is the absolute temperature.

II. Approach to Equilibrium I

We shall not give a general proof of this here but we shall restrict ourselves to a proof for the *spatially homogeneous case* where $f(\mathbf{rv}t)$ depends only on v and not on r .

1. Proof of H-theorem for $f(vt)$

H-Theorem. For any $f(vt)$ that is a solution of the spatially homogeneous Boltzmann equation, the function H (defined below) never increases with time.

Proof. Define a function H by*

$$H = \int f(vt) \ln f(vt) dv \quad (6.7)$$

Then using eq. (6.1), that $\partial f / \partial t = 0$ and that $\partial(f f dv) / \partial t = 0$, one has

$$\frac{dH}{dt} = \int \frac{\partial f}{\partial t} \ln f dv = \int dv \int dv_1 \int db b \int d\psi g \ln f [f'f'_1 - f\bar{f}] \quad (6.8)$$

Here we have written f for $f(\mathbf{rv}t)$, f' for $f(\mathbf{rv}'t)$, etc. Interchanging v and v_1 on the r.h.s. of eq. (6.8), and adding the equation thus obtained to eq. (6.8), one has

$$\frac{dH}{dt} = \frac{1}{2} \int dv \int dv_1 \int db b \int d\psi g \ln f\bar{f}_1 [f'f'_1 - f\bar{f}] \quad (6.9)$$

Interchanging (v, v_1) and (v', v'_1) on the r.h.s. of eq. (6.9), using the fact that $dv dv_1 = dv' dv'_1$ and that $g = g'$, and adding the equation so obtained to eq. (6.9), one has

$$\frac{dH}{dt} = \frac{1}{4} \int dv \int dv_1 \int db b \int d\psi g \ln \left(\frac{f\bar{f}_1}{f'f'_1} \right) [f'f'_1 - f\bar{f}] \leq 0 \quad (6.10)$$

as the r.h.s. of eq. (6.10) is always ≤ 0 .

From eq. (6.10) it follows that $dH/dt \leq 0$ for all t , thus H can never increase.

* The symbol H does not stand for capital h but for capital (greek) eta, thus emphasizing the connection with the entropy $\eta \equiv S$. In fact, in equilibrium, when $f(v, t) = f_M$, $H^{eq} = -S/k + \text{constant}$.

2. Proof of Approach of f to Equilibrium

H will continue to decrease* until finally, as $t \rightarrow \infty$, $dH/dt = 0$ for all \mathbf{v} , \mathbf{v}_1 , \mathbf{b} , ψ (that is, for all possible binary collisions), and

$$f(\mathbf{v})f(\mathbf{v}_1) = f(\mathbf{v}')f(\mathbf{v}'_1) \quad (6.11)$$

Taking the logarithm of both sides of eq. (6.11), we have

$$\ln f(\mathbf{v}) + \ln f(\mathbf{v}_1) = \ln f(\mathbf{v}') + \ln f(\mathbf{v}'_1) \quad (6.12)$$

This equation shows that $\ln f(\mathbf{v}t)$ is an additive collisional invariant, that is, the total of $\ln f$ summed over the two colliding molecules before—and after—a collision is the same. Since the *only* independent additive collisional invariants are the number (1), the momentum ($m\mathbf{v}$), and the (kinetic) energy ($\frac{1}{2}mv^2$) of a molecule, $\ln f$ must be a linear combination of the five invariants mentioned, that is,

$$\ln f(\mathbf{v}) = a + \mathbf{b} \cdot \mathbf{v} + \frac{1}{2}cmv^2$$

or also

$$f(\mathbf{v}) = a \exp[-\frac{1}{2}c(\mathbf{v} - \mathbf{b}/c)^2] \quad (6.13a)$$

where a , \mathbf{b} , and c are constants. By using the definitions:

$$n = \int f(\mathbf{v}) d\mathbf{v} \quad (6.14a)$$

$$n\mathbf{u} = \int f(\mathbf{v})\mathbf{v} d\mathbf{v} = 0 \quad (6.14b)$$

$$\frac{3}{2}nkT = \int f(\mathbf{v})\frac{1}{2}m(\mathbf{v} - \mathbf{u})^2 d\mathbf{v} \quad (6.14c)$$

one can relate the five constants a , \mathbf{b} , and c to the usual constants density (n), average velocity (\mathbf{u}), and temperature (T) that characterize thermal equilibrium. One obtains

$$f(\mathbf{v}) = f_M(\mathbf{v}) = n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(- \frac{m\mathbf{v}^2}{2kT} \right) \quad (6.13b)$$

where we have set $\mathbf{u} = 0$.

* That H cannot decrease indefinitely is due to the fact that H must have a minimum value. For if this were not so, and H could be $-\infty$, then this would mean that $\int f \ln f d\mathbf{v}$ diverges. This could only be so if, for $v \rightarrow \infty$ and $f \rightarrow 0$, $\ln f$ would go faster to $-\infty$ than $f \rightarrow 0$. This can only be so if $\ln f$ goes to infinity faster than v^2 , as $\int f \frac{1}{2}mv^2 d\mathbf{v}$ —the total kinetic energy of the gas—must certainly exist. However, if $\ln f \sim v^n$, with $n > 2$, then $f \sim \exp(-v^n)$, and H will certainly exist!

II. Approach to Equilibrium I

Therefore, f approaches, through binary collisions, monotonically to the equilibrium distribution function given by eq. (6.13). Strictly speaking, f only obtains f_M after an infinite time. For all practical purposes, however, f will equal f_M to a very good approximation after very many collisions have occurred, that is, when $t \gg t_{mf}$, the mean-free time.

The proof of the approach to equilibrium in the spatially inhomogeneous case proceeds in a similar fashion. One considers, instead of the H -function defined by eq. (6.7), the function $H' = \int H d\mathbf{r}$ (f depends on \mathbf{r} , \mathbf{v} , and t now).

(1) First one proves an H -theorem for H' . dH'/dt contains now contributions from the streaming—as well as from the collision—term in the Boltzmann equation. Since the contribution from the streaming term can be shown to vanish, H' changes only through collisions. One can show, by using the preceding arguments, that H' never increases (H -theorem).

(2) The proof of the approach of f to equilibrium now proceeds in two steps. (a) First, one has from the H -theorem that f , in the course of time, will approach monotonically a *local* Maxwell-distribution function $f_0(\mathbf{v})$, which is given by an expression of the same form as that on the r.h.s. of eq. (6.13), except that now n , \mathbf{u} , and T will depend on \mathbf{r} and t (the average velocity \mathbf{u} is in general not zero), that is,

$$f_0(\mathbf{v}) = n(\mathbf{r}t) \left(\frac{m}{2\pi kT(\mathbf{r}t)} \right)^{3/2} \exp \left(- \frac{m\mathbf{V}^2(\mathbf{r}t)}{2kT(\mathbf{r}t)} \right) \quad (6.15a)$$

Here, the peculiar velocity, $\mathbf{V}(\mathbf{r}t)$, defined by

$$\mathbf{V}(\mathbf{r}t) = \mathbf{v} - \mathbf{u}(\mathbf{r}t) \quad (6.15b)$$

is the velocity of a molecule at \mathbf{r} relative to the average velocity \mathbf{u} at \mathbf{r} .

In eq. (6.15) the functions $n(\mathbf{r}, t)$, $\mathbf{u}(\mathbf{r}, t)$, and $T(\mathbf{r}, t)$ are the local number density, the local velocity, and the local temperature of the gas, respectively. These are defined by [compare eq. (6.14)]

$$n(\mathbf{r}t) = \int f(\mathbf{r}\mathbf{v}t) d\mathbf{v} \quad (6.16a)$$

$$n(\mathbf{r}t)\mathbf{u}(\mathbf{r}t) = \int f(\mathbf{r}\mathbf{v}t)\mathbf{v} d\mathbf{v} \quad (6.16b)$$

$$\frac{3}{2}n(\mathbf{r}t)kT(\mathbf{r}t) = \int f(\mathbf{r}\mathbf{v}t) \frac{m\mathbf{V}^2}{2} d\mathbf{v} \quad (6.16c)$$

(b) Then, to determine the \mathbf{r} and t dependence of the five functions

n , u , and T , one substitutes f_0 into the Boltzmann equation. Since $J(f_0 f_0)$ vanishes, the change of f_0 with time is given by the streaming term only. One can then demonstrate that the only solution of this equation for f_0 is the (total) equilibrium distribution function f_M given by eq. (6.6)* so that n and T are independent of r and t and $u = 0$.

In reality, the approach to total equilibrium in a spatially inhomogeneous system will also go in two steps, as is suggested by the proof just given. First, in a time of the order of the mean-free time t_{mfp} , the system approaches monotonically a state of local equilibrium in which the velocities are already distributed according to a Gaussian (Maxwellian) distribution, except that the five constants which characterize this (local) velocity equilibrium vary still with position and time. Then, in a time of the order of the traversal time of the container t_{macro} [see (B)], it approaches (not necessarily monotonically) the state of total equilibrium where also all spatial variations have disappeared. For the first step, one should emphasize the word "approach": The state of local equilibrium is never reached, but only attained to a first approximation. This follows from the fact that f_0 is not a solution of the full Boltzmann equation but only of the equation $J(f f) = 0$. The function f_M , however, is a solution of the full Boltzmann equation!

B. THE CHAPMAN-ENSKOG SOLUTION (7,8)

Although the H-theorem establishes once and for all the fact that a gas will approach equilibrium, it does not provide information about how this approach to equilibrium proceeds, other than that this approach proceeds in two steps. In fact, it seems that in order to obtain more information, one would have to obtain a solution of the Boltzmann equation itself; a formidable undertaking in view of the fact that the equation is a non-linear integrodifferential equation in six variables, in addition to the time. However, for the case that the gas is *near equilibrium*, Chapman and Enskog have been able to avoid this formidable problem. They have been able, by obtaining a *special* solution of the Boltzmann equation, to gain more information about the approach to equilibrium, while at the same

* In the (more realistic) case that an outside force field $F(r)$ is present, an additional term appears in the equation for f_0 . But for some very special (academic) cases, the only solution of this equation for f_0 is the Maxwell-Boltzmann distribution function: $f_{MB} = f_M \exp(-V(r)/kT)$ where $V(r)$ is the potential of the outside force field $F(r)$: $F(r) = -\partial V(r)/\partial r$.

II. Approach to Equilibrium I

time establishing the connection with the equations of hydrodynamics. The details of their work will be given in the next section. In this section we will sketch the general ideas behind the Chapman-Enskog solution of the Boltzmann equation.

The Boltzmann equation describes mathematically the time evolution of a dilute gas. However, physically, it will be clear that the time evolution of the gas, or of any system for that matter, will be dominated by the characteristic relaxation times of the system. In our case of a dilute gas there are three characteristic relaxation times which are related to three basic lengths in the gas: the (effective) range of the intermolecular forces r_0 , the mean-free path l , and a macroscopic length for example, the length L of the vessel, which contains the gas.* For a dilute gas that obeys the Boltzmann equation, one has

$$r_0 \ll l \ll L$$

The characteristic times t_c , t_{mfp} , and t_{macro} , corresponding to r_0 , l , and L , respectively, can be obtained by dividing r_0 , l , and L by a characteristic velocity. It is convenient to choose the velocity of sound for this: $v_s \approx 10^4$ cm sec⁻¹. Then one obtains the following table which is characteristic for a dilute gas at 0°C and 1 atm pressure.

TABLE I

	r_0	l	L
cm	10^{-8}	10^{-7}	1
	t_c	t_{mfp}	t_{macro}
sec	10^{-12}	10^{-10}	10^{-4}

For our case, therefore, the three characteristic times are far apart, viz:

$$t_c \ll t_{mfp} \ll t_{macro}$$

The first inequality: $t_c \ll t_{mfp}$, expresses the fact that the gas is *dilute* and that each molecule spends most of its time in a free flight which is occasionally interrupted by a (binary) collision. For, replacing $t_c \ll t_{mfp}$ by the original inequality $r_0 \ll l$ and using that $l \sim 1/nr_0^2$ one sees this

* This is only true if the intermolecular forces are short ranged. For Coulomb forces for example, where $\phi(r) \sim 1/r$, such a distinction is not meaningful.

implies that $nr_0^3 \ll 1$. The second inequality, $t_{mtp} \ll t_{macr}$ permits—for a large class of initial states—to distinguish in the time evolution of the gas towards thermal equilibrium two steps or stages:

(a) For times $0 < t \leq t_{mtp}$ a *kinetic stage*, where for an adequate description in its approach to equilibrium, the gas has to be described by $f(\mathbf{rv}t)$ which has to be obtained from a *general* solution of the Boltzmann equation;

(b) For times $t \gg t_{mtp}$, a *hydrodynamical stage*, where the gas, for an adequate description in its approach to equilibrium, can be described by the five hydrodynamical quantities $n(\mathbf{r}t)$, $\mathbf{u}(\mathbf{r}t)$ and $T(\mathbf{r}t)$, instead of by $f(\mathbf{rv}t)$. The five hydrodynamical quantities are defined by eq. (6.16) and are, therefore, related to the first five moments of f with respect to \mathbf{v} only. Therefore, it is clear that the hydrodynamical description of the gas by means of n , \mathbf{u} , and T in the hydrodynamical stage is much simpler than the description by means of the full distribution function $f(\mathbf{rv}t)$ in the kinetic stage. The approach of the gas to equilibrium is thus accompanied by a simplification of the description of the gas.

The existence of these two stages, in particular the hydrodynamical stage, can be established on physical grounds by the following argument.

For almost any initial state at $t = 0$, every molecule in the volume element dr around \mathbf{r} will have collided several times after a time $t \gg t_{mtp}$. During each collision the velocities of the colliding molecules change enormously due to the strong intermolecular forces. As a consequence, all functions depending on the velocities of the molecules at \mathbf{r} , in particular $f(\mathbf{rv}t)$, will change very rapidly with time. However, five functions, viz., $n(\mathbf{r}t)$, $\mathbf{u}(\mathbf{r}t)$, and $T(\mathbf{r}t)$, will not change at all because of collisions. This is so because the number, momentum, and energy of the molecules are conserved during collisions. Therefore, as far as collisions are concerned, n , \mathbf{u} , and T at \mathbf{r} will *not change at all* during the time t and will remain constant during all the collisional turmoil that is going on at \mathbf{r} during the time t . As a consequence, all the rapidly changing quantities at \mathbf{r} (and in particular f) will adapt themselves to the "prevailing" n , \mathbf{u} , and T at \mathbf{r} during the time t , and will have become *dependent* on n , \mathbf{u} , and T after a time $t \gg t_{mtp}$.

The preceding argument only considered the change of n , \mathbf{u} , and T due to collisions at \mathbf{r} , but neglected the change of n , \mathbf{u} , and T due to spatial inhomogeneities in the gas at \mathbf{r} , that is, due to the gradients of n , \mathbf{u} , and T at \mathbf{r} . Now, if the variations of n , \mathbf{u} , and T over a mean-free path are small—as is almost always the case—then one can in first approximation neglect the change of n , \mathbf{u} , and T due to spatial inhomogeneities at \mathbf{r} ,

II. Approach to Equilibrium I

and the preceding argument still applies. More precisely: if one calls any of the macroscopic quantities (n , \mathbf{u} , or T) M , then the argument applies if the relative change of M over a mean-free path is small; in other words, if

$$\mu = \frac{1}{M} l \frac{\Delta M}{L} = \frac{1}{M} l \text{ grad } M \ll 1$$

where ΔM is the difference in M over L .^{*} Therefore, one would indeed expect on physical grounds that after a time $t \gg t_{mtp}$, the time evolution of the gas can be adequately described by the time evolution of the five hydrodynamical quantities alone, and that the full $f(\mathbf{rv}t)$ is not needed anymore.

Continuing this physical discussion of the time evolution of the gas, one would expect after a time $t \gg t_{macr}$, when every molecule has traversed the vessel many times, that all spatial inhomogeneities have been equalized and that the hydrodynamical state of *local* equilibrium of the gas which is characterized by the five functions $n(\mathbf{r}t)$, $\mathbf{u}(\mathbf{r}t)$, $T(\mathbf{r}t)$ will have gone over into the final state of *total* (thermal) equilibrium of the gas, characterized by two parameters n and T alone. We remark that the approach of the gas to equilibrium is then again accompanied by an increasing simplification of the description:

$$\begin{array}{ccccc} \text{stage:} & \text{Kinetic} & & \text{Hydrodynamical} & & \text{Equilibrium} \\ \text{description:} & f(\mathbf{rv}t) & \xrightarrow[t \gg t_{mtp}]{} & n(\mathbf{r}t), \mathbf{u}(\mathbf{r}t), T(\mathbf{r}t) & \xrightarrow[t \gg t_{macr}]{} & n, T \end{array}$$

A different way of expressing the existence of two stages in the approach of a dilute gas to equilibrium is to say that one can distinguish in the approach of such a gas to equilibrium two processes:

(a) A *fast* process on the time scale of t_{mtp} which establishes (in first approximation at least), after a time $t \gg t_{mtp}$, a *local* (velocity) equilibrium;

(b) A *slow* process on the time scale of t_{macr} which leads, after a time $t \gg t_{macr}$, to *total* equilibrium. The uniformity parameter μ is proportional to the ratio of these two characteristic times, viz:

$$\mu \sim t_{mtp}/t_{macr}$$

^{*} If the system is uniform and $\Delta M = 0$, then $\mu = 0$. Thus μ measures the deviations from spatial homogeneity, and is consequently called the uniformity parameter.

III. Approach to Equilibrium II—The Chapman-Enskog Solution: Connection with Hydrodynamics (9)

In this section we shall make the physical results of the previous section mathematically more precise. We shall study the approach to equilibrium of the gas in the hydrodynamical stage, that is, for times $t \gg t_{\text{mfp}}$ when the gas is already near equilibrium. As argued in the previous section, we can look then for special solutions of the Boltzmann equation which are such that f , as far as its time dependence is concerned, is completely determined by its first five moments: n , \mathbf{u} , and T alone. Thus

$$f(\mathbf{rv}t) \xrightarrow{t \gg t_{\text{mfp}}} f(\mathbf{rv} | n\mathbf{u}T) \quad (6.17)$$

so that

$$\begin{aligned} \frac{\partial f(\mathbf{rv}t)}{\partial t} \rightarrow \frac{\partial f(\mathbf{rv} | n\mathbf{u}T)}{\partial t} &= \frac{\partial f(\mathbf{rv} | n\mathbf{u}T)}{\partial n} \frac{\partial n}{\partial t} \\ &+ \frac{\partial f(\mathbf{rv} | n\mathbf{u}T)}{\partial \mathbf{u}} \cdot \frac{\partial \mathbf{u}}{\partial t} + \frac{\partial f(\mathbf{rv} | n\mathbf{u}T)}{\partial T} \frac{\partial T}{\partial t} \end{aligned} \quad (6.18)$$

Here $f(\mathbf{rv} | n\mathbf{u}T)$ indicates that the t -dependence of f is through $n(\mathbf{r}t)$, $\mathbf{u}(\mathbf{r}t)$ and $T(\mathbf{r}t)$.

Assuming eq. (6.17) one can actually find a special solution of the Boltzmann equation for f of this form in successive approximations by expanding $f(\mathbf{rv} | n\mathbf{u}T)$ in powers of the uniformity parameter μ ($\mu \ll 1$):

$$f(\mathbf{rv} | n\mathbf{u}T) = f_0(\mathbf{rv} | n\mathbf{u}T) + \mu f_1(\mathbf{rv} | n\mathbf{u}T) + \mu^2 f_2(\mathbf{rv} | n\mathbf{u}T) + \dots \quad (6.19)$$

In this expansion the parameter μ is meant as a parameter indicating the order of magnitude of the terms. It is used like the parameter λ in the Rayleigh-Schrödinger perturbation theory in quantum mechanics to classify terms according to their magnitude. Like λ , μ is set equal to one at the end of the calculation.

Substituting this expansion in the r.h.s. of the Boltzmann equation and using that $\partial f_0 / \partial \mathbf{r} \sim \mu$, one obtains the following μ -expansion for the r.h.s. of the Boltzmann equation (6.1)*:

$$J(f_0 f_0) + \mu \left[-\mathbf{v} \cdot \frac{\partial f_0}{\partial \mathbf{r}} + \{J(f_0 f_1) + J(f_1 f_0)\} \right] + \mu^2 \dots + \dots \quad (6.20)$$

* As it has not been assumed that the \mathbf{r} dependence of f should be only through n , \mathbf{u} , and T , it has been tacitly assumed in obtaining (6.20) that the variation of f with \mathbf{r} through any explicit dependence of f on \mathbf{r} (that is, not via n , \mathbf{u} , or T) does not exceed the variation of f with \mathbf{r} through n , \mathbf{u} , and T .

III. Approach to Equilibrium II

To obtain a μ -expansion of the l.h.s. of the Boltzmann equation one needs to know, in view of eq. (6.18), the μ -expansion of $\partial n / \partial t$, $\partial \mathbf{u} / \partial t$, and $\partial T / \partial t$. Now equations can be obtained for these quantities by multiplying both sides of the Boltzmann equation with 1 , \mathbf{v} , and $\frac{1}{2} m v^2$, respectively, and integrating over \mathbf{v} . Using then that the collision term, $J(f'f)$, does not contribute due to the conservation of number, momentum and energy in a collision, one obtains the following five conservation equations which express the conservation of number, momentum, and energy, respectively, during the time-evolution of the gas:

Equation of Continuity (Conservation of Number):

$$\frac{dn}{dt} = -n \frac{\partial u_x}{\partial r_x} = -n D_{xx} \quad (6.21a)$$

Equation of Motion (Conservation of Momentum):

$$nm \frac{du_i}{dt} = - \frac{\partial \mathcal{P}_{ix}^K}{\partial r_x} \quad (i = x, y, z) \quad (6.21b)$$

Equation of Energy (Conservation of Energy):

$$n \frac{d\epsilon^K}{dt} = \frac{3}{2} nk \frac{dT}{dt} = - \frac{\partial J_x^K}{\partial r_x} - \mathcal{P}_{\alpha\beta}^K D_{\alpha\beta} \quad (6.21c)$$

Here d/dt is the substantial time derivative,

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \text{grad} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}} = \frac{\partial}{\partial t} + u_x \frac{\partial}{\partial r_x}$$

The summation convention is used so that if two identical greek indices occur, it is understood that a summation over the x -, y -, and z -components has to be carried out.

The pressure tensor \mathcal{P}_{ij}^K is given by

$$\mathcal{P}_{ij}^K = \mathcal{P}_{ij}^K(\mathbf{r} | f) = \int f m v_i v_j dv \quad (i, j = x, y, z) \quad (6.22)$$

while the heat flux vector J_i^K is given by

$$J_i^K = J_i^K(\mathbf{r} | f) = \int f \frac{1}{2} m v^2 v_i dv \quad (i = x, y, z) \quad (6.23)$$

The superscript K indicates that in the computation of the pressure tensor \mathcal{P}_{ij} and the heat flux vector J_i , only kinetic contributions due to

the transitional motion of the molecules have been taken into account. The rate of strain tensor D_{ij} is defined by

$$D_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right) \quad (6.24)$$

We obtain from eqs. (6.21) $\partial n/\partial t$, $\partial u/\partial t$, and $\partial T/\partial t$ in a power series in μ by expanding \mathcal{P}_{ij}^K and J_i^K in powers of μ , by substituting the μ -expansion eq. (6.19) for f into the expressions (6.22) and (6.23), respectively, and collecting all terms of the same order in μ . One obtains then the following μ -expansion for $\partial n/\partial t$, $\partial u/\partial t$, and $\partial T/\partial t$:

$$\frac{\partial n}{\partial t} = \mu \left(\frac{\partial n}{\partial t} \right)_0 + \mu^2 \cdots + \cdots = \mu \left(-u_\alpha \frac{\partial n}{\partial r_\alpha} - n \frac{\partial u_\alpha}{\partial r_\alpha} \right) \cdots \quad (6.25a)$$

$$\frac{\partial u_i}{\partial t} = \mu \left(\frac{\partial u_i}{\partial t} \right)_0 + \mu^2 \cdots + \cdots = \mu \left(-u_\alpha \frac{\partial u_i}{\partial r_\alpha} - \frac{1}{nm} \frac{\partial \mathcal{P}_{i\alpha,0}^K}{\partial r_\alpha} \right) \cdots \quad (6.25b)$$

$$\frac{\partial T}{\partial t} = \mu \left(\frac{\partial T}{\partial t} \right)_0 + \mu^2 \cdots + \cdots = \mu \left(-u_\alpha \frac{\partial T}{\partial r_\alpha} - \frac{2}{3nk} \frac{\partial J_{\alpha,0}^K}{\partial r_\alpha} - \mathcal{P}_{\alpha\beta,0}^K D_{\alpha\beta} \right) \cdots \quad (6.25c)$$

Here one has used that

$$\mathcal{P}_{ij}^K = \mathcal{P}_{ij,0}^K + \mu \mathcal{P}_{ij,1}^K + \cdots \quad (6.26)$$

with

$$\mathcal{P}_{ij,0}^K = \int f_0 m V_i V_j d\mathbf{v} \quad (6.26a)$$

$$\mathcal{P}_{ij,1}^K = \int f_1 m V_i V_j d\mathbf{v} \quad (6.26b)$$

and that

$$J_i^K = J_{i,0}^K + \mu J_{i,1}^K + \cdots \quad (6.27)$$

with

$$J_{i,0}^K = \int f_0 \frac{1}{2} m \mathbf{V}^2 V_i d\mathbf{v} \quad (6.27a)$$

$$J_{i,1}^K = \int f_1 \frac{1}{2} m \mathbf{V}^2 V_i d\mathbf{v} \quad (6.27b)$$

(We have omitted the appendage ($i = x, y, z$) or ($i, j = x, y, z$) from the preceding equations. From now on it is always assumed that the summation of i and j runs over the axes x, y , and z .)

Using now eqs. (6.18) and (6.25)–(6.27), one obtains the following

III. Approach to Equilibrium II

μ -expansion for the l.h.s. of the Boltzmann equation (6.1):

$$\mu \left[\frac{\partial f_0}{\partial n} \left(\frac{\partial n}{\partial t} \right)_0 + \frac{\partial f_0}{\partial \mathbf{u}} \cdot \left(\frac{\partial \mathbf{u}}{\partial t} \right)_0 + \frac{\partial f_0}{\partial T} \left(\frac{\partial T}{\partial t} \right)_0 \right] + \mu^2 \cdots + \cdots \quad (6.28)$$

Equating then the coefficients of equal powers of μ on the l.h.s. and the r.h.s. of the Boltzmann equation, one obtains, with eqs. (6.20) and (6.28), the following set of equations for f_0, f_1, \dots :

$$O(\mu^0): \quad J(f_0 f_0) = 0 \quad (6.29a)$$

$$O(\mu): \quad J(f_0 f_1) + J(f_1 f_0) = \frac{\partial f_0}{\partial n} \left(\frac{\partial n}{\partial t} \right)_0 + \frac{\partial f_0}{\partial \mathbf{u}} \cdot \left(\frac{\partial \mathbf{u}}{\partial t} \right)_0 + \frac{\partial f_0}{\partial T} \left(\frac{\partial T}{\partial t} \right)_0 + \mathbf{v} \cdot \frac{\partial f_0}{\partial \mathbf{r}} \quad (6.29b)$$

The eqs. (6.29) can be solved successively for f_0, f_1, \dots

A. SOLUTION OF THE f_0 EQUATION

The equation for f_0 is identical with that obtained from the equation $dH/dt = 0$ in the spatially inhomogeneous case. Consequently, the equation has the local Maxwell distribution function f_0 , given by the eq. (6.15a) as a solution.

Equation (6.29a) is satisfied by any function of the form (6.15a), with n, u , and T arbitrary functions of \mathbf{r} and t , and not necessarily the local density, velocity, and temperature, respectively. We choose however—in accordance with the considerations of the previous section— n, u , and T as the local hydrodynamical quantities, and this will enable us to obtain a well-defined solution scheme for the eqs. (6.29).

Because the n, u , and T for the gas also follow from the eqs. (6.16), these same equations must be satisfied if f_0 instead of f is used. Thus, one can require from all higher approximations, f_l with $l \geq 1$, that

$$\int f_l d\mathbf{v} = 0 \quad (6.30a)$$

$$\int f_l V_i d\mathbf{v} = 0 \quad (6.30b)$$

$$\int f_l \frac{1}{2} m \mathbf{V}^2 d\mathbf{v} = 0 \quad (6.30c)$$

Therefore, since $J(f\bar{f})$ is the collision term, one sees that (as was anticipated in the previous section on physical grounds) f does approach through collisions the local equilibrium distribution function f_0 .

With $f = f_0$, one can now evaluate the r.h.s. of the conservation equations; in particular, one can compute \mathcal{P}_{ij}^K and J_i^K . In doing so one obtains the *Euler equations of hydrodynamics* for an ideal gas:

$$\frac{dn}{dt} = -n \frac{\partial u_\alpha}{\partial r_\alpha} = -n D_{\alpha\alpha} \quad (6.31a)$$

$$nm \frac{du_i}{\partial t} = - \frac{\partial p^K}{\partial r_i} \quad (6.31b)$$

$$n \frac{d\epsilon^K}{dt} = \frac{3}{2} nk \frac{dT}{dt} = -p^K \frac{\partial u_\alpha}{\partial r_\alpha} = -p^K D_{\alpha\alpha} \quad (6.31c)$$

Here one has used that, with $f = f_0$, the pressure tensor is of the form:

$$\mathcal{P}_{ij,0}^K = p^K \delta_{ij} \quad (6.32a)$$

Here p^K is the hydrostatic pressure given by the ideal gas law:

$$p^K = nkT \quad (6.32b)$$

while the heat flux vector J_i^K is given by

$$J_{i,0}^K = 0 \quad (6.33)$$

and $n\epsilon^K$, the local (kinetic) energy density, is given by the ideal gas expression:

$$n\epsilon^K = \frac{3}{2} nkT \quad (6.34)$$

One might wonder why the ideal gas laws are obtained for the pressure and the energy density, in spite of the fact that the Boltzmann equation contains contributions from binary collisions through the collision term $J(f\bar{f})$. The reason is that the collision term in the form of eq. (6.1b) does not contribute to the conservation equations. In order to obtain contributions to the pressure and the energy density from binary collisions, the *difference in position* of the two colliding molecules must be taken into account in the collision term, that is, in $J(f\bar{f})$ the two f 's should *not* be taken both at the same position.

We see that in local equilibrium ($f = f_0$), the thermodynamic functions such as the pressure and the energy are the same functions of $n(\mathbf{r}t)$ and $T(\mathbf{r}t)$, as they are in (total) equilibrium of n and T .*

B. SOLUTION OF THE f_1 EQUATION (LINEARIZED BOLTZMANN EQUATION THEORY)

Using eqs. (6.25) and (6.31)–(6.33), the r.h.s. of eq. (6.29b) can be determined. This leads to the following linear inhomogeneous integral

* Combining eqs. (6.31a) and (6.31c), one obtains the adiabatic equation of state: $d(nT^{-5/3})/dt = 0$.

III. Approach to Equilibrium II

equation for f_1 :

$$J(f_0 f_1) + J(f_1 f_0) = f_0 \left[\left(\frac{mV^2}{2kT} - \frac{5}{2} \right) V_\alpha \frac{\partial \ln T}{\partial r_\alpha} + \left(\frac{mV_\alpha V_\beta}{kT} - \frac{mV^2}{3kT} \delta_{\alpha\beta} \right) D_{\alpha\beta} \right] \quad (6.35)$$

Introducing the function Φ_1 , through the equation:

$$f_1(\mathbf{r}\mathbf{v} | n\mathbf{u}T) = f_0(\mathbf{r}\mathbf{v} | n\mathbf{u}T) \Phi_1(\mathbf{r}\mathbf{v} | n\mathbf{u}T) \quad (6.36)$$

eq. (6.35) can be transformed into a linear inhomogeneous integral equation for Φ_1 :

$$I(\Phi_1) = \left(\frac{mV^2}{2kT} - \frac{5}{2} \right) V_\alpha \frac{\partial \ln T}{\partial r_\alpha} + \left(\frac{mV_\alpha V_\beta}{kT} - \frac{mV^2}{3kT} \delta_{\alpha\beta} \right) D_{\alpha\beta} \quad (6.37)$$

Here the (symmetric) linear binary collision operator I is defined by

$$I(\Phi_1) = \int d\mathbf{v}_1 f_0(v_1) \int db \int d\psi [\Phi_1(\mathbf{v}') + \Phi_1(\mathbf{v}_1) - \Phi(\mathbf{v}) - \Phi_1(\mathbf{v}_1)] \quad (6.38)$$

where, on the r.h.s. we have only indicated the velocity dependence of Φ_1 .

According to the theory of integral equations, the inhomogeneous integral equation [eq. (6.37)] for Φ_1 is soluble if its r.h.s. is orthogonal to the solutions of the associated homogeneous integral equation:

$$I(\Phi_1) = 0 \quad (6.39)$$

Since this integral equation has as independent solutions only the five collisional invariants 1, mV , and $\frac{1}{2}mV^2$,* one easily convinces oneself that the solubility conditions for the integral equation (6.37) are fulfilled.†

The general solution to eq. (6.37) can now be written as:

general solution = particular solution plus 5 constants times 5 solutions of homogeneous equation.

To make the general solution of eq. (6.37) definite, one fixes the five constants by the five conditions for $l = 1$ [eq. (6.30)]:

$$\int f_1 d\mathbf{v} = \int f_1 V d\mathbf{v} = \int f_1 V^2 d\mathbf{v} = 0 \quad (6.40)$$

* The five collisional invariants 1, mV , $\frac{1}{2}mV^2$ are linear combinations of the five collisional invariants 1, mv , $\frac{1}{2}mv^2$ mentioned before.

† As the r.h.s. of eq. (6.37) is an evaluation of $\partial f_0 / \partial t + \mathbf{v} \cdot \partial f_0 / \partial \mathbf{r}$ to $O(\mu)$, the orthogonality conditions are nothing else than Euler's equations of hydrodynamics!

We have now established the *existence* of a *unique solution* of the integral equation (6.37) for Φ_1 .

One can find the *form* of Φ_1 by using that the integral operator I is a linear operator, that the r.h.s. of eq. (6.37) is linear in the gradients, and that the gradients of T and \mathbf{u} have a different tensorial character. It can then be shown that Φ_1 is of the following general form:

$$\Phi_1(\mathbf{rv} | n\mathbf{u}T) = -A_\alpha(\mathbf{V}) \frac{\partial \ln T}{\partial r_\alpha} - B_{\alpha\beta}(\mathbf{V}) D_{\alpha\beta} \quad (6.41)$$

and, by substituting (6.41) for Φ_1 into the integral equation (6.37), that $A_i(\mathbf{V})$ and $B_{ij}(\mathbf{V})$ satisfy the integral equations:

$$I(A_i) = -\left(\frac{mV^2}{2kT} - \frac{5}{2}\right) V_i \quad (6.42a)$$

$$I(B_{ij}) = -\left(\frac{mV_i V_j}{kT} - \frac{mV^2}{3kT} \delta_{ij}\right) \quad (6.42b)$$

Furthermore, it follows from the eqs. (6.42) that $A_i(\mathbf{V})$ is a vector, while $B_{ij}(\mathbf{V})$ is a traceless tensor because the tensor on the r.h.s. of eq. (6.42) is traceless. As \mathbf{V} is the only vector available, the functions $A_i(\mathbf{V})$ and $B_{ij}(\mathbf{V})$ must be of the form*:

$$A_i(\mathbf{V}) = A(V) V_i \quad (6.43a)$$

$$B_{ij}(\mathbf{V}) = B(V) \left[\frac{mV_i V_j}{kT} - \frac{mV^2}{3kT} \delta_{ij} \right] \quad (6.43b)$$

Because of eq. (6.40), the (scalar) function A is subject to the condition:

$$\int f_0(V) A(V) V^2 dv = 0 \quad (6.44)$$

while the function $B(V)$ is subject to no restrictions.†

The functions $A(V)$ and $B(V)$ can be found from the integral equations (6.42a) and (6.42b), respectively. Before we do so, we first derive the form of the conservation equations with $f = f_0 + f_1$. We remark that as $f_1 = f_0 \Phi_1$, we have from eqs. (6.41), (6.37), and (6.30):

(1) $f_1 \sim \partial T / \partial r_i$, and $\partial u_i / \partial r_j$, that is, $f_1 \sim \text{grad } T$ and $\text{grad } \mathbf{u}$.

* For a more elaborated discussion of this point, see reference 10.

† The first two conditions in eq. (6.40) are *automatically* fulfilled for $A_i(\mathbf{V})$, while all three conditions in eq. (6.40) are *automatically* fulfilled for $B_{ij}(\mathbf{V})$. This follows from the general form of $A_i(\mathbf{V})$ and $B_{ij}(\mathbf{V})$, respectively [see eq. (6.43)].

(2) f_1 is independent of n .

The last result follows from the fact that the l.h.s. of the integral equation (6.37) must be independent of n as is the r.h.s.

With $f = f_0 + f_1$, one can evaluate the r.h.s. of the conservation equations. In particular, one can compute \mathcal{P}_{ij}^K and J_i^K . In so doing one obtains the *Navier-Stokes* equation of hydrodynamics:

$$\frac{dn}{dt} = -n \frac{\partial u_\alpha}{\partial r_\alpha} = -n D_{\alpha\alpha} \quad (6.44a)$$

$$nm \frac{du_i}{dt} = -\frac{\partial p^K}{\partial r_i} - \frac{\partial \mathcal{P}_{ia,1}^K}{\partial r_\alpha} \quad (6.44b)$$

$$n \frac{d\epsilon^K}{dt} = \frac{3}{2} nk \frac{dT}{dt} = -\frac{\partial J_{a,1}^K}{\partial r_\alpha} - (p^K \delta_{\alpha\beta} + \mathcal{P}_{\alpha\beta,1}^K) D_{\alpha\beta} \quad (6.44c)$$

Here we have used that, with $f = f_0 + f_1$, the pressure tensor \mathcal{P}_{ij} is of the form:

$$\mathcal{P}_{ij}^K = \mathcal{P}_{ij,0}^K + \mathcal{P}_{ij,1}^K = p^K \delta_{ij} + \mathcal{P}_{ij,1}^K \quad (6.45a)$$

Here the off-diagonal part $\mathcal{P}_{ij,1}^K$ of \mathcal{P}_{ij}^K obeys *Newton's law of viscous flow*:

$$\mathcal{P}_{ij,1}^K = -2\eta^K (D_{ij} - \frac{1}{3} D_{\alpha\alpha} \delta_{ij}) \quad (6.45b)$$

while the heat flux vector J_i^K obeys *Fourier's law of heat conduction*:

$$J_i^K = J_{i,1}^K = -\lambda^K \frac{\partial T}{\partial r_i} \quad (6.46)$$

The coefficients η^K in eq. (6.45a) and λ^K in eq. (6.46) are the transport coefficients: the shear viscosity and the heat conductivity, respectively, of the dilute gas.* They depend on the temperature T but not on the density n because f_1 is independent of n .

Using eqs. (6.26b), (6.36), (6.41), and (6.43b)—and the fact that averages of odd functions of \mathbf{V} vanish when evaluated with $f_0(V)$ (which is symmetric in \mathbf{V})—one obtains the expression for η^K :

$$\eta^K(T) = \frac{m^2}{15kT} \int f_0(V) V^4 B(V) dv \quad (6.47)$$

Similarly, using eqs. (6.27b), (6.36), (6.41), (6.43b), and (6.44) one obtains

* For the bulk viscosity see Chapter 7.

the expression for λ^K :

$$\lambda^K(T) = \frac{k}{3} \sqrt{\frac{m}{2kT}} \int \left(\frac{mV^2}{2kT} - \frac{5}{2} \right) V^2 A(V) f_0 dv \quad (6.48)$$

To obtain the explicit temperature dependence of η^K and λ^K one must know $A(V)$ and $B(V)$, and therefore solve the integral equations, (6.42), for $A(V)$ and $B(V)$. A solution of these integral equations can be obtained by expanding the functions $A(V)$ and $B(V)$ in terms of a complete set of orthogonal functions of V . A convenient set is formed by the Sonine polynomials, which are eigenfunctions of the linear integral operator I for the case of Maxwell molecules, that is, for the case of the intermolecular potential $\phi(r) \sim 1/r^4$. The convenience of the Sonine polynomials expansion, even for realistic (nonMaxwell) molecules, is due to the fact that the r.h.s. of each of the eqs. (6.42) can be directly related to a Sonine polynomial in V . For *Maxwell molecules* this implies that only one Sonine polynomial is needed for the computation of $A(V)$ and $B(V)$, that is, for the computation of η^K and λ^K . In principle, for a *general intermolecular potential*, all polynomials of a complete (infinite) set of Sonine polynomials are needed to compute $A(V)$ and $B(V)$. To determine $A(V)$ or $B(V)$ then, one has to solve an infinite set of linear equations for the coefficients of the Sonine polynomials. This set of equations can be solved successively by taking into account more and more coefficients. In practice, the expansion seems to converge rapidly, and when one restricts oneself to one coefficient—that is, to one Sonine polynomial—in the expansion of $A(V)$ or $B(V)$, we already get results for η^K and λ^K , which are correct to a few per cent! In fact, in so doing, the following expressions are obtained for η^K and λ^K , valid for a general (short-ranged) intermolecular potential (I):

$$\eta^K(T) = \frac{5}{8} \frac{kT}{\Omega^{(2,2)}(T)} \quad (6.49)$$

$$\lambda^K(T) = \frac{5}{2} c_{\phi} \eta^K(T) = \frac{25}{16} \frac{kT}{\Omega^{(2,2)}(T)} c_{\phi} \quad (6.50)$$

Here

$$\Omega^{(2,2)}(T) = \frac{1}{2\sqrt{\pi}} \left(\frac{m}{4kT} \right)^{7/2} \int_0^{\infty} \exp \left(-\frac{mg^2}{4kT} \right) g^7 Q^{(2)}(g) dg \quad (6.51)$$

is a weighted (with g^7) temperature average—with a Maxwell distribution function—over the transport cross section $Q^{(2)}(g)$, characteristic for

viscosity and heat conductivity. The cross section $Q^{(2)}(g)$ is defined by

$$Q^{(2)}(g) = \int_0^{\infty} db b \int_0^{2\pi} d\psi (1 - \cos^2 \chi) \quad (6.52)$$

and is a weighted average [with $(1 - \cos^2 \chi)$] of the differential cross section $b db d\psi$. The angle $\chi = \chi(b, g)$ is the scattering angle in the binary collision, characterized by the impact parameter b and the relative velocity g . This angle depends, apart from on b and g , also on the intermolecular potential field $\phi(r)$, and it is in this manner that the transport coefficients, η^K and λ^K depend on the intermolecular potential field. The term $c_{\phi} = \frac{3}{2} k/m$, is the specific heat of a monatomic gas per unit mass.

If evaluated numerically for a realistic intermolecular potential $\phi(r)$ as, for example, for the 12-6 Lennard-Jones potential, the values of η^K and λ^K given by eq. (6.49) and eq. (6.50), respectively, agree very well with experiment over a wide range of temperatures (compare Section IV, Subsection 3c, and Chapter 9).

As a function of b , g , and $\phi(r)$, χ follows from the mechanics of two particles in infinite space, and is given by the expression:

$$\chi = \pi - 2 \int_0^{z_0} \frac{dz}{\left[1 - z^2 - \frac{4}{mg^2} \phi(b/2) \right]^{1/2}}$$

where z_0 is the smallest root of the equation obtained when the expression under the square root in the denominator is set equal to zero. If the molecules are point centers of force and if the (repulsive) intermolecular potential $\phi(r) = \kappa r^{-n}$, then χ reduces to

$$\chi = \pi - 2 \int_0^{z_0} \frac{dz}{1 - z^2 - \frac{4\kappa}{mg^2} \left(\frac{2}{b} \right)^n}$$

where z_0 is the real positive root of the equation:

$$1 - z^2 - \frac{4\kappa}{mg^2} \left(\frac{2}{b} \right)^n = 0$$

For this case one easily sees that the transport cross section

$$Q^{(2)}(g) \sim g^{1-n}$$

so that

$$\Omega^{(2,2)}(T) \sim T^{1/2-n}$$

and

$$\eta^K(T) \sim T^{1/2+2/n}$$

The temperature dependence of η^K reflects therefore *directly* the strength of the intermolecular repulsion $n!$ (12).

IV. Discussion

In this section we shall discuss a number of points connected with the results obtained in the previous section.

(1) We first want to verify that the expansion parameter μ —used to indicate the order of magnitude of the terms in the Chapman-Enskog expansion—is indeed the parameter defined in Section II (13). Using eq. (6.19) [see remark about μ following eq. (6.19)] and (6.36), we have

$$\mu = \frac{f_1}{f_0} = \frac{f_0 \Phi_1}{f_0} = \Phi_1$$

Now in case there is, say, a temperature gradient:

$$\Phi_1 = -A_\alpha(V) \cdot \frac{\partial \ln T}{\partial r_\alpha}$$

where $A_i(V)$ satisfies [compare eq. (6.42a)] the integral equation:

$$I[A(V)V_i] = -\left(\frac{mV^2}{2kT} - \frac{5}{2}\right)V_i$$

Because the operator $I \sim nQ$, where Q is the total scattering cross section, one must have that $A \sim 1/nQ \sim l$. Therefore, indeed:

$$\Phi_1 = \frac{l}{T} \frac{\partial T}{\partial x} = \frac{l}{T} \frac{\Delta T}{L} = \mu$$

if the temperature gradient is in the x -direction. A similar discussion can be given in case there is a velocity gradient.

(2) In the preceding section, we have derived for times $t \gg t_{mt}$, that the approach of a dilute gas to equilibrium is governed by the hydrodynamical equations. We remark that the hydrodynamical equations were obtained from a molecular point of view and not on the basis of continuum

mechanics, as was the case in Chapter 2. For that reason, we were able to obtain the explicit n and T dependence of the thermodynamic (p^K , ϵ^K), as well as of the transport properties (η^K , λ^K) of the gas in terms of the intermolecular forces.

(3) As far as experimental verification of the results obtained in the previous section is concerned: (a) the density independence of η and λ over a wide range of densities—corresponding roughly to pressures of 0.01 atm to about 5 atm (this depends also on the temperature)—has been very well confirmed for a larger number of gases; (b) the Eucken relation: $\lambda/\eta c_v = 5/2$ agrees very well with experiment for monatomic gases (that is, the noble gases); and (c) the temperature dependence of the transport coefficients η^K and λ^K for a realistic intermolecular potential presents a sensitive test of the theory of the (linearized) Boltzmann equation.

All these points are further discussed in Chapter 9. Here we would like to say a few words about point (c). A comparison between theory and experiment can be made by using the law of corresponding states. This law holds for all substances that can be described by an intermolecular potential which can be characterized by two parameters (for example, by the 12-6 Lennard-Jones potential characterized by ϵ and σ).^{*} All physical quantities can then be reduced, that is, be made dimensionless, with the help of the three molecular parameters, m , σ , and ϵ .

The law of corresponding states says that if the molecules of these substances move according to the laws of classical mechanics, any functional relationship between physical quantities that holds for any one of these substances can be transformed into a relationship valid for *all* these substances, provided that the physical quantities occurring in that relationship are replaced by the corresponding reduced quantities.

All the noble gases can be very well described by a 12-6 Lennard-Jones potential. It follows then, for dilute gases, that the properly reduced viscosity coefficient should be the *same* function of the reduced temperature T^* for *all* noble gases.[†]

Indeed, using the expression (6.49) with eq. (6.51) for η^K , one obtains the relation:

$$\eta^{K*}(T^*) = \frac{5}{8} \frac{T^*}{\Omega^{(2,2)*}(T^*)} \quad (6.53)$$

^{*} The *form* of the potential must be the same for all substances, as for example, a 12-6 Lennard-Jones potential; the ϵ and σ values will be different, of course, for substances which are not isotopes.

[†] For the light noble gases, however, see point (4) in this section.

where

$$\eta^{K*} = \frac{\eta^{K\sigma}}{(m\epsilon)^{1/2}} \quad (6.54)$$

and

$$T^* = kT/\epsilon \quad (6.55)$$

$$\Omega^{(2,2)*}(T^*) = \Omega^{(2,2)}(kT/\epsilon) \frac{1}{\sigma^2} \left(\frac{m}{\epsilon}\right)^{1/2} \quad (6.56)$$

Using for each noble gas values of ϵ and σ determined from the temperature dependence of the second virial coefficient,† the experimental values of η , when properly reduced according to eqs. (6.54) and (6.55), indeed yield a universal curve for η^* as a function T^* (see Fig. 2) (14). At high temperatures, where the repulsive part $\sim 1/r^{12}$ of the intermolecular potential dominates the scattering of the noble gas atoms, η^* should behave $\sim T^{*2/3}$. Or, the slope of the plotted curve for large values of T^* should be

$$\frac{d \ln \eta^*/(T^*)^{1/2}}{d \ln T^*} = \frac{1}{6} \quad (6.57)$$

which is to a good approximation, so.

The good agreement over a wide range of temperatures for a variety of substances (including even some with only approximately spherically symmetric intermolecular potentials like O_2 , N_2 , H_2) is not only a check on the validity of the Boltzmann equation and the Chapman-Enskog solution, but also, of course, on the 12-6 Lennard-Jones potential as an effective intermolecular potential.

(4) Curves for some *light* gases (D_2 , H_2 , 4He , 3He) are also drawn in Fig. 2. These show deviations from the law of corresponding states, especially at low temperatures (15). This is due to the fact that, for light molecules, quantum mechanical deviations from the classical motion become important at low temperatures. The reason for this is that, at low temperatures, the de Broglie wavelength associated with a light molecule, λ_{mol} , becomes appreciable compared to the size of the molecule (that is, to σ) so that quantum-mechanical diffraction effects become important, and deviations from the classical behavior occur. The larger λ_{mol}/σ is the larger the deviations will be. Now:

$$\lambda_{mol} \sim \frac{h}{\bar{p}_{mol}} \sim \frac{h}{\sqrt{mkT}} \quad (6.58)$$

† For our purposes this procedure is sufficient. See, however, Chapter 9, Section II.

where \bar{p}_{mol} is an average momentum of a molecule. Therefore, the quantum mechanical deviations from the classical behavior due to diffraction effects are determined by

$$\frac{\lambda_{mol}}{\sigma} = \frac{h}{\sigma\sqrt{mkT}} = \frac{\Lambda^*}{\sqrt{T^*}} \quad (6.59)$$

where the quantum mechanical parameter Λ^* is given by

$$\Lambda^* = \frac{h}{\sigma\sqrt{m\epsilon}} \quad (6.60)$$

Thus, at a given reduced temperature T^* , the quantum deviations from the classical (corresponding states) behavior will be larger as the value of

TABLE 2

Λ^*	3He	4He	H_2	D_2
	3.09	2.68	1.73	0.865

Λ^* is larger, that is, the lighter and smaller the molecule is and the weaker the intermolecular potential. Table 2 lists the value of Λ^* for various light gases, and it is seen in Fig. 2 that the deviations from the classical behavior do indeed increase with the value of Λ^* at a given T^* .

In addition to diffraction effects, quantum-mechanical statistics effects will also occur if λ_{mol} is of the order of the average distance between the molecules. At the densities and temperatures in which we are interested, these statistics effects are of importance only during the collision of molecules.*

Both kinds of quantum mechanical effects require a modification of the Stosszahl-Ansatz. In our case, the only change one has to apply is that the classical differential cross section is replaced by the quantum-mechanical differential cross section:

$$b \, db \, d\psi = I(g, \chi) \sin \chi \, d\chi \quad (6.61)$$

Here $I(g, \chi)$ can be found by computing the quantum-mechanical phase shifts $\eta_l(k)$ characteristic of the relative motion of two molecules with

* For sufficiently low T , however, λ_{mol} will become of the order of the average intermolecular distance, so that statistics effects occur due to a quantum degeneracy of the gas as a whole (see reference 15).

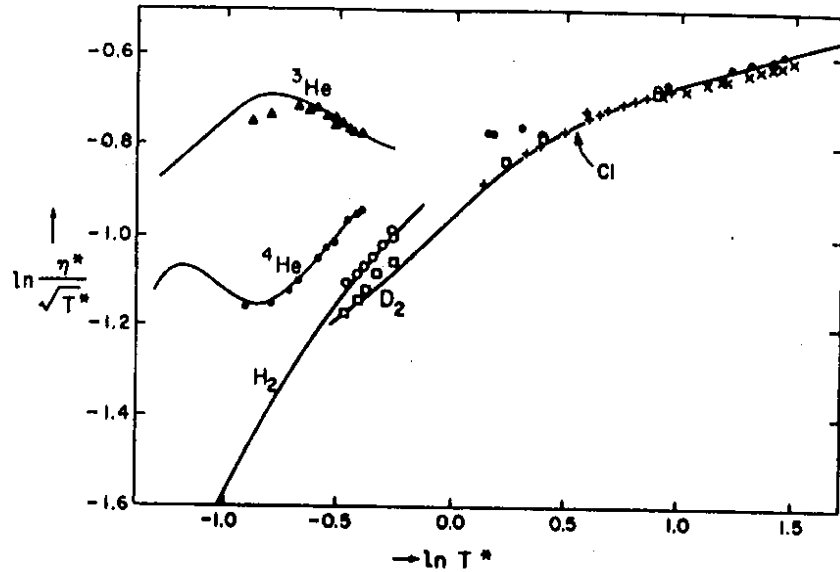


Fig. 2. Reduced viscosity coefficients from eqs. (6.49), (6.53), and (6.56) plotted against reduced temperature: $\ln \eta^*/\sqrt{T^*}$ versus $\ln T^*$. Cl is the classical curve. Experimental points: \blacktriangle ^3He ; \bullet ^4He ; \circ H_2 ; \square D_2 ; \times Ne; $+$ A.

relative energy $\hbar^2 k^2/2m = \frac{1}{2}mg^2$ and angular momentum $[l(l+1)\hbar]^2 = \frac{1}{2}mgb$. As the $\eta_l(k)$ depend implicitly on Λ^* , the transport coefficients η^* and λ^* will also depend on Λ^* .

The statistics effects during the collision make necessary the use of wavefunctions, which are properly symmetrized with respect to the coordinates of the two colliding particles. Thus for ^4He and H_2 , which consist of an even number of elementary particles (neutrons, protons, and electrons) and follow Bose-Einstein statistics,[†] only wavefunctions symmetrical in the coordinates of the two colliding particles should be used. This implies that only $\eta_l(k)$ with even l can be used in the computation of $I(g, \chi)$. For ^3He which consists of an odd number of elementary particles, has a spin of $\frac{1}{2}$, and follows Fermi-Dirac statistics,[†] wavefunctions both symmetric and antisymmetric in the coordinates of the colliding particles can occur. This implies that $\eta_l(k)$, with both even and odd l , are used in the computation of $I(g, \chi)$. This leads to large differences in η^* for ^3He and ^4He , at the same T^* . These differences due to quantum statistics come in addition to those due to the difference in Λ^* which are a consequence of the difference in mass (ϵ and σ are the same for ^3He and ^4He since they are isotopes.)

[†] This is based on a theorem of Ehrenfest and Oppenheimer (16). This theorem states that composite particles like atoms or molecules consisting of a number of elementary particles can be treated as point particles following a definite quantum

(5) As we pointed out before, the Chapman-Enskog solution of the Boltzmann equation is a special solution to which, presumably, the general solution of the Boltzmann equation approaches for a large class of initial conditions. One can ask: What is the nature of this approach? It seems certain that the approach is exponential with a characteristic time of the order of t_{mfp} , that is, $\sim \exp(-t/t_{\text{mfp}})$. This is made plausible by Grad's thirteen moment expansion of f (17). Grad considered special solutions of the Boltzmann equation where it is assumed that f depends on thirteen—instead of five—moments of f ; that is, f depends, in addition to its five moments with l , v , and v^2 , also on those with v_x^2 , v_y^2 , $v_x v_y$, $v_x v_z$, $v_y v_z$, and $v^2 v$. The special solution of the Boltzmann equation, f_G , which Grad obtained on the basis of this assumption seems to be more accurate than the Chapman-Enskog solution $f_{\text{Ch-E}} \equiv f(\mathbf{rv} | nuT)$, discussed in Section III. However, Grad was able to show that the additional eight moments, when computed with the (more accurate) f_G decay exponentially in a time of the order of t_{mfp} to the values they would have had if they had been computed directly on the basis of the Chapman-Enskog $f_{\text{Ch-E}}$ using five moments only! This illustrates again the possible simplification of the description of the gas after a time $t \gg t_{\text{mfp}}$ because the "extra information" which these eight additional moments contain, in addition to n , \mathbf{u} , and T , has disappeared after $t \gg t_{\text{mfp}}$.

(6) The Euler and the Navier-Stokes equations are the hydrodynamical equations which correspond to taking $f = f_0$ or $f = f_0 + f_1$, respectively, in the general conservation equations. They can be trusted to describe adequately the approach of the gas to equilibrium, only as long as $\mu \ll 1$, that is, as long as the (relative) variation of the macroscopic variables over l is small. If one has, however, a rarefied gas where l is not $\ll L$, or if a sound wave propagates through the gas with a wavelength λ_s such that the (relative) variations of the macroscopic variables over λ_s are not small, then corrections to the Navier-Stokes equations involving f_2 , etc., will become important. The hydrodynamical equations obtained using f_2 , in addition to f_0 and f_1 —that is, using $f = f_0 + f_1 + f_2$ in the

statistics in all processes where the internal structure of the composite particles does not play a role. In the case of the noble gases this means that the theorem applies as long as the temperature of the gas does not approach the ionization temperature of the gas atoms. The theorem further states that the point particles obey Bose-Einstein statistics if they consist of an even number of elementary particles (for example, ^4He) and Fermi-Dirac statistics if they consist of an odd number of elementary particles (for example, He).

conservation equations—are called the *Burnett equations*. The hydrodynamical equations obtained using f_3 as well could be called the super-Burnett equations, and so on. Clearly to the μ -expansion [eq. (6.19)] of f there corresponds a whole hierarchy of hydrodynamical equations, which involve increasingly higher gradients of n , u , and T . The Euler- and Navier-Stokes equations are only the first two sets of equations.

A check on the validity of the Burnett equations can be made by studying the dispersion and the absorption of sound in a dilute gas. For long wavelengths: $\lambda_s \gg l$, the dispersion and the absorption of sound as a function of λ_s , obtained from the (linearized) Navier-Stokes equations, agree well with experiment. With decreasing λ_s , however, deviations are observed which can be accounted for by using the (linearized) Burnett equations instead of the (linearized) Navier-Stokes equations (18). Thus in this case the Burnett equations are able to describe the behavior of the gas under conditions in which μ is not very much less than one.

V. The Connection with Irreversible Thermodynamics

One of the basic assumptions of irreversible thermodynamics is that the same thermodynamic laws and relations hold for the local thermodynamic quantities in a system which is (in first approximation) in local equilibrium, as hold for the ordinary thermodynamic quantities in a system which is in total equilibrium. In particular, it is assumed that the so-called Gibbs relation (19)

$$T ds = de + pd(1/\rho), \quad (6.62a)$$

valid in (total) equilibrium, is still valid in the form:

$$T \frac{ds}{dt} = \frac{de}{dt} + p \frac{d(1/\rho)}{dt} \quad (6.62b)$$

in local equilibrium.

Most of the results of irreversible thermodynamics are obtained from this equation by using it to define appropriate fluxes J_i ($i = 1, 2, \dots, n$) and associated forces X_i ($i = 1, 2, \dots, n$), which are such that linear relationships exist between them, viz.,

$$J_i = \sum_{j=1}^n L_{ij} X_j \quad (i = 1, 2, \dots, n) \quad (6.63)$$

for which the matrix of the coefficients L_{ij} is symmetric, that is,

$$L_{ij} = L_{ji} \quad (i, j = 1, 2, \dots, n) \quad (6.64)$$

In (6.62a), s , e , and $1/\rho$ are the specific entropy, energy, and volume, respectively, while in (6.62b), s , e , and $1/\rho$ are the specific *local* entropy, energy, and volume, respectively, which depend on r as well as on t . The term d/dt is the substantial time derivative defined before. The total energy has been defined by eq. (2.30), only here we have set the kinetic energy from the center-of-gravity motion and the external potential energy equal to zero, therefore $e = \epsilon^k/m$.

Onsager was the first to prove that fluxes and forces could be defined for which the *Onsager reciprocal relations* hold [see eq. (6.64) and Chapter 5]. The proof was based on the hypothesis that the decay of microscopic fluctuations of a system in equilibrium follows the macroscopic linear laws [eq. (6.63)] and, in addition, only used microscopic reversibility, that is, the time-reversal invariance of the microscopic equations of motion [cf. eqs. (6.5a,b)]. For a single gas of the kind considered here, no Onsager relations [eq. (6.64)] exist. Therefore, in this section we shall only prove that eqs. (6.62) and (6.63) are valid for a dilute gas, on the basis of the Chapman-Enskog solution of the Boltzmann equations. A proof of this was given for the first time by Prigogine (20). For a mixture of two (dilute) gases there is a relation of the form eq. (6.64) which expresses the equality of the thermal diffusion coefficient and the Dufour coefficient. A proof of this relation, as well as the eqs. (6.62b) and (6.63) for the case of a binary mixture, is presented in Appendix A of Chapter 7. (A proof of the Onsager reciprocal relation between the diffusion coefficients in a multicomponent mixture has been given by de Groot and Mazur (21).)

A. PROOF OF THE GIBBS RELATION

(a) To prove the Gibbs relation on the basis of the Chapman-Enskog solution of the Boltzmann equation, and to define fluxes and forces J_i and X_i , respectively, it is convenient to transform the eq. (6.62b) into another, but equivalent, equation [eq. (6.69a,b)]. This is done with the help of (the always valid) general conservation laws for mass density ρ ,

($\rho = nm$) momentum, and energy*:

$$\frac{d\rho}{dt} = -\rho D_{\alpha\alpha} \quad (6.65a)$$

$$\rho \frac{du_i}{dt} = -\frac{\partial \mathcal{P}_{i\alpha}}{\partial r_\alpha} \quad (6.65b)$$

$$\rho \frac{de}{dt} = -\frac{\partial J_\alpha}{\partial r_\alpha} - \mathcal{P}_{\alpha\beta} D_{\alpha\beta} \quad (6.65c)$$

With eqs. (6.65a) and (6.65c), eq. (6.62) can be written in the form:

$$\rho \frac{ds}{dt} = -\frac{1}{T} \frac{\partial J_\alpha}{\partial r_\alpha} - \frac{1}{T} \mathcal{P}_{\alpha\beta,1} D_{\alpha\beta} \quad (6.66)$$

where $\mathcal{P}_{i,1}$ is defined by

$$\mathcal{P}_{i,1} = \mathcal{P}_{i1} - p\delta_{i1} \quad (6.67)$$

Introducing the entropy flux vector $j_i(s)$ by the relation

$$j_i(s) = \frac{J_i}{T} \quad (6.68)$$

eq. (6.66) can be written in the form of a balance equation:

$$\rho \frac{ds}{dt} = -\frac{\partial j_\alpha(s)}{\partial r_\alpha} + \sigma(s) \quad (6.69a)$$

where the entropy production $\sigma(s)$ is given by

$$\sigma(s) = -\frac{1}{T} J_\alpha \frac{\partial \ln T}{\partial r_\alpha} - \frac{1}{T} \mathcal{P}_{\alpha\beta,1} D_{\alpha\beta} \quad (6.69b)$$

In the following we shall prove eqs. (6.68) and (6.69a,b), rather than eq. (6.62b).

(b) In order to prove a relation concerning the rate of change of the local entropy of a dilute gas we must first have a definition of the entropy of such a gas in terms of the distribution function f just as, say, the (local) energy density ϵ^K was defined by eq. (6.16c).

* The Euler- and Navier-Stokes equations of hydrodynamics obtained before follow from the general conservation laws [Eqs. (6.65)] under the special conditions that the pressure tensor \mathcal{P}_{ij} and the heat flux vector J_i satisfy eqs. (6.32) and (6.33), or (6.45) and (6.46), respectively.

One defines the entropy density S_v^K by

$$S_v^K = -kH_v^K \quad (6.70)$$

where

$$H_v^K = H_v^K(\mathbf{r} | f) = -\int d\mathbf{v} f(\mathbf{rv}t) [1 - \ln f(\mathbf{rv}t)] \quad (6.71)$$

This definition of S_v^K is such that in local equilibrium, when $f = f_0$, the local Maxwell distribution function, S_v^K , is the same function of n and T as it is in equilibrium, and reduces to the known expression for an ideal gas

$$S_v^{i.e.} = -kH^K(\mathbf{r} | f_0) = -3n \ln \lambda - \frac{5}{2}n - n \ln n$$

where $\lambda = (2\pi mkT)^{-1}$. As before, the superscript K reminds us of the fact that for the dilute gas only kinetic contributions to S and H are considered.

We now calculate dH^K/dt from eq. (6.71). Using the Boltzmann equation (6.1), one obtains

$$\frac{dH_v^K}{dt} = -\int d\mathbf{v} \ln f V_\alpha \frac{\partial f}{\partial r_\alpha} + \int d\mathbf{v} \ln f J(f) \quad (6.72)$$

The two terms in the r.h.s. are treated as follows:

(1) The first term on the r.h.s. of eq. (6.72) can be rewritten with eq. (6.15b) in the form:

$$-\int d\mathbf{v} \ln f V_\alpha \frac{\partial f}{\partial r_\alpha} = -\frac{\partial}{\partial r_\alpha} \left[\int d\mathbf{v} f \ln f V_\alpha \right] - \int d\mathbf{v} f \ln f D_{\alpha\alpha} + \int d\mathbf{v} \frac{\partial f}{\partial r_\alpha} V_\alpha \quad (6.73)$$

Using eq. (6.19), expanding the logarithm, and keeping only terms in this expansion up to $O(\mu)$, one has, with eq. (6.27),

$$-\frac{\partial}{\partial r_\alpha} \left[\int d\mathbf{v} f \ln f V_\alpha \right] = \frac{\partial}{\partial r_\alpha} \left(\frac{J_\alpha^K}{kT} \right) \quad (6.74)$$

Using eqs. (6.71) and (6.16a) one also has that

$$-\int d\mathbf{v} f \ln f D_{\alpha\alpha} = -(H_v^K + n) D_{\alpha\alpha} \quad (6.75)$$

while with eqs. (6.15b) and (6.16a,b):

$$\int d\mathbf{v} \frac{\partial f}{\partial r_\alpha} V_\alpha = n D_{\alpha\alpha} \quad (6.76)$$

Adding eqs. (6.74), (6.75), and (6.76) yields for eq. (6.73):

$$-\int dv \ln f V_\alpha \frac{\partial f}{\partial r_\alpha} = \frac{\partial}{\partial r_\alpha} \left(\frac{J_\alpha^K}{kT} \right) - H_\alpha^K D_{\alpha\alpha} \quad (6.77)$$

(2) The second term on the r.h.s. of eq. (6.72) can be reduced with eq. (6.19); expanding the logarithm, keeping only terms of $O(\mu)$ in this expansion, one obtains

$$\int dv \ln f J(f) = \int dv \left[\ln f_0 + \frac{f_1}{f_0} \right] [J(f_0 f_1) + J(f_1 f_0)] \quad (6.78)$$

One easily verifies, using, for example, eq. (6.15a), that the terms on the r.h.s. of eq. (6.78) containing $\ln f_0$ vanish. Then, by using eqs. (6.36) and (6.41), the integral equations (6.42), and eqs. (6.26) and (6.27), one finds for the r.h.s. of eq. (6.78), the following result:

$$\int dv \ln f J(f) = \frac{J_\alpha^K}{kT} \frac{\partial \ln T}{\partial r_\alpha} + \frac{\mathcal{P}_{\alpha\beta,1}^K}{kT} D_{\alpha\beta} \quad (6.79)$$

Using eqs. (6.77) and (6.79) and the fact that for any thermodynamic quantity its specific value A_ρ (that is, its value per unit mass) and its density A_v (that is, its value per unit volume) are related by

$$\rho \frac{dA_\rho}{dt} = \frac{dA_v}{dt} + A_v D_{\alpha\alpha}$$

Equation (6.72) can be written in the form:

$$\rho \frac{dH_\rho^K}{dt} = - \frac{\partial j_\alpha(H_\rho^K)}{\partial r_\alpha} + \sigma(H_\rho^K) \quad (6.80)$$

where

$$j_i(H_\rho^K) = \frac{J_i^K}{kT} \quad (6.80b)$$

and

$$\sigma(H_\rho^K) = \frac{J_\alpha^K}{kT} \frac{\partial \ln T}{\partial r_\alpha} + \frac{\mathcal{P}_{\alpha\beta,1}^K}{kT} D_{\alpha\beta} \quad (6.80c)$$

or*:

$$\sigma(H_\rho^K) = \frac{J_\alpha^K}{kT} \frac{\partial \ln T}{\partial r_\alpha} + \frac{\mathcal{P}_{\alpha\beta,1}^K}{kT} D_{\alpha\beta} \quad (6.80d)$$

* In the transition from eq. (6.80c) to eq. (6.80d), one has used the fact that, as \mathcal{P}_{ij}^K is a traceless tensor, the inner product of the tensor D_{ii} and the traceless tensor $\mathcal{P}_{ii,1}$ is equal to the inner product of the traceless tensor $(D_{ii} - \frac{1}{3}D_{ii}\delta_{ii})$ and the traceless tensor $\mathcal{P}_{ii,1}$ (22).

Using eq. (6.70), one sees that eq. (6.80) is identical with (6.69). Therefore, with (6.80), (6.69), and ultimately (6.62), have been proven for a dilute gas.

According to the principles of irreversible thermodynamics, the expression (6.69b) is of the form:

$$\sigma = - \frac{1}{T} \sum_i J_i X_i$$

This defines the fluxes J_i and forces X_i for which the linear relations (6.63) should hold.

By comparing with the eqs. (6.69b), (6.70), and (6.80d), and by using eqs. (6.45b) and (6.46) for the fluxes J_i^K and $\mathcal{P}_{ij,1}^K$, respectively, one sees that the linear relations (6.63) are indeed satisfied and, in fact, are nothing else but Newton's law of viscous flow and Fourier's law of heat conduction.

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CHAPTER

7

 THE KINETIC THEORY OF MODERATELY DENSE GASES,*

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I. Introduction and Approach to Equilibrium I (6)

In order to explain the experimental facts observed in moderately dense gases on the basis of the dynamics of the molecules in μ -space, one needs a generalization of the Boltzmann equation to higher densities.

To this day no one has been able to generalize Boltzmann's procedure, that is, to look at the motion of the molecules in μ -space and compute the change of f with time by generalizing the Stoszahl-Ansatz to include the effect of triple and higher order collisions.

Therefore, one has had to *derive* the generalized Boltzmann equation in a systematic way, that is, one has had to start from the basic equation of statistical mechanics, the Liouville equation, expand in some way in the density, obtain in first approximation the Boltzmann equation, and then, in the next approximation, a correction term incorporating the effect of triple collisions, and so on.

Bogolubov was the first one to carry out this program. His work has greatly influenced the development of kinetic theory in the last ten years. Very recently it has been found that his ideas cannot be entirely correct and *only* lead to a correct derivation of the Boltzmann equation and to the first correction (due to triple collisions) to this equation. Since we shall restrict ourselves here to this case and since, moreover, we believe that the

* For general background, see references (1-5).