

THE STATISTICAL MECHANICS
OF
NON-EQUILIBRIUM PHENOMENA

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1. The problem of Boltzmann.

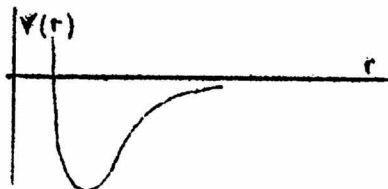
How can one possibly "explain" the irreversible behaviour of thermodynamical system from a strictly reversible mechanical model?

This will be the theme for my first set of lectures. It is properly called the problem of Boltzmann, since he struggled with it during his whole life. Of course after his work and the further developments by Gibbs, Einstein, Smoluchowski, Ehrenfest and others, the essential features of the solution have become quite clear and well known. However, it may be good to review the situation, because especially for non-ideal gases the concrete questions of how to deduce the non-equilibrium properties of the system from its molecular constitution are still far from a satisfactory solution.

I will restrict myself by using :

(a) Classical mechanics. It is time that the quantum mechanics, especially thru the act of measurement, adds a new feature (perhaps a "time" irreversibility) to the problem, and it is also true that often the quantum theory is formally simpler, but I think the essential questions arise already in the classical theory, and since I am most familiar with it I will restrict myself to the classical theory.

(b) Point molecules interacting thru short-range central forces which have the additivity property (no many-body forces). One must think of a van der Waals or molecular potential but I will often consider the case of repulsive forces only (elastic spheres or repulsion $\sim 1/r^5$, the Maxwell molecules).



2. The kinetic method and the H-theorem.

The central question is the explanation of the second law of thermodynamics; however, it is simple to see that if one can explain one typical irreversible event, and specifically the approach to thermal equilibrium, then everything follows. This is the reason why the proof of the Maxwell-Boltzmann distribution law has such importance. Can one show for a gas that the distribution functions

$$f(t, \vec{r}, \vec{v}) d\vec{r} d\vec{v} = \text{number of molecules in } \mu\text{-space cell } d\vec{r} d\vec{v}$$

approaches in course of time the M. B. distribution

$$f_0 = A e^{-\frac{1}{kT} \left\{ \frac{mv^2}{2} + U(\vec{r}) \right\}}$$

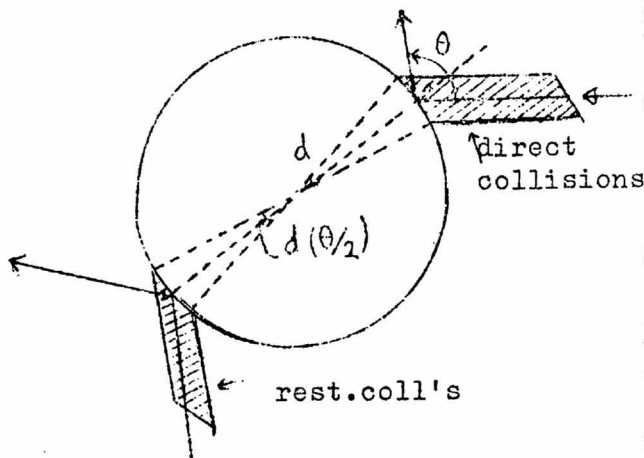
where U = potential of outside forces, and A is determined by total number of molecules?

I now have to remind you of the so-called kinetic proof of Boltzman
The starting point is the basic continuity. Equation :

$$\frac{Df}{Dt} \equiv \frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_r f + \vec{a} \cdot \nabla_v f = \int d\vec{v}' \int d\Omega I(g, \theta) (f' f'_1 - f f_1) \quad (1)$$

where \vec{a} = acceleration of outside forces; index 1 and prime refers to the velocity variable only, so that $f_1 \equiv f(r, v_1, t)$ etc.;
 $(\vec{v}, \vec{v}'_1) \leftrightarrow (\vec{v}'_1, \vec{v}_1)$ are the direct and restituting collisions;

$g \equiv |\vec{v}_1 - \vec{v}| = |\vec{v}'_1 - \vec{v}'|$; $I(g, \theta)$ is differential cross section for turning the relative velocity over an angle θ "in solid angle $d\Omega$ ". For instance for elastic spheres :



Volume cylinder :
 $g d^2 \cdot \cos \frac{\theta}{2} \cdot 2\pi \sin \frac{\theta}{2} d \frac{\theta}{2} d\phi$

$$= g \frac{d^2}{4} d\Omega$$

$$\text{So } I(g, \theta) = \frac{d^2}{4}$$

For Maxwell molecules, force law k/r^5 , one finds :

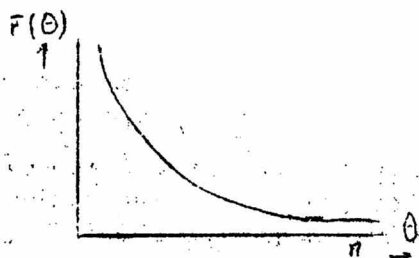
$$g I(g, \theta) = \sqrt{\frac{2k}{m}} F(\theta),$$

independent of g . $F(\theta)$ is complicated, is monotonic decreasing; for small θ ,

$$F(\theta) = \frac{\sqrt{3\pi}}{15} \frac{1}{\theta^{5/2}} \left(1 + \frac{35}{24\pi} \theta + \dots \right)$$

It is well approximated by :

$$F(\theta) \sim \frac{\sqrt{3\pi}}{\sqrt{2}} \frac{1}{\sin^5 \sqrt{\theta/2}}$$



The usual justification of (1) is familiar; f changes for two reasons : the streaming in μ -space, and the collisions. The collision term is crucial; it produces the irreversibility. It is based on the Stoszzahl Ansalz, which is an assumption of a non-mechanical nature. It is where the statistics comes in! Note the following limitations :

(a) Some uniformity is assumed. Strictly, the positions of the colliding molecules should not be the same, and variations over distances of the order of a mean free path are perhaps already doubtful. Thus very fast varying phenomena as high frequency sound (freq. of order of collision frequency, or wavelength of order of free path) may not be correctly described.

(b) Only binary collisions are assumed, and no correlations of the velocity directions is taken into account, although forces are present.

Clearly Boltzmann had some sort of a successive approximation idea in mind. Already the description of the state of the gas by $f(\vec{r}, \vec{v}, t)$ implies that in zero. approx. the forces are neglected and the gas is ideal. The collisions depending on pairs of molecules are the next approximation, and are responsible for the transport phenomena (viscosity, heat cond.) and also for the first deviation (2nd virial coefficient) of the ideal gas law.

The approach to equilibrium is proved by means of the H-theorem. Boltzmann defines :

$$H(t) \equiv \iint F \log f \, d\vec{r} \, d\vec{v} \quad (2)$$

and he proves

$$1) \frac{dH}{dt} = \iint \frac{\delta f}{\delta t} \log f \, d\vec{r} \, d\vec{v} = \left(\frac{dH}{dt} \right)_{\text{streaming}} + \left(\frac{dH}{dt} \right)_{\text{collisions}}$$

Due to the streaming of the H function does not change. This is a special use of a general theorem. If there are no collisions (so no forces) then the gas is an ensemble (copies of identical systems each in different states of motion and each sending one point into the phase space; systems are now the molecules, phase space is p-space). The Liouville theorem states that the streaming in such a case is as an incompressible fluid (or is an "equivolumic transformation"). Therefore any integral of the form

$$\left\{ \dots \right\} F(p) \, dq_1 \dots dp_n$$

must be independent of the time.

2) Due to the collisions H always decreases, and dH/dt is only zero if for all possible collisions :

$$f f_1 = f' f'_1 \quad (3)$$

This determines the dependence of f on the velocities; $\log f$ must be a linear function of the quantities conserved in a collision, which leads to

$$f = A e^{-\beta \frac{m}{2} \left\{ (u-u_s)^2 + \dots \right\}} \quad (4)$$

In every volume elem. in velocity space the approach to (4) is monotonic. The approach to the M. B. distribution in coordinate space is much more complicated. In (4) the quantities A, u_0, v_0, w_0 can still be functions of x, y, z and t , which must follow from

$$\frac{\delta f}{\delta t} + \vec{v} \cdot \nabla_r f + \vec{a} \cdot \nabla_v f = 0 \quad (5)$$

Only for sufficiently general outside forces (which include shape of the vessel) is the solution unique and corresponds to $\beta = \text{const}$, $u_0 = v_0 = w_0 = 0$ and $A = A_0 e^{-\beta U}$. For special forces there are a host of special solutions, which can even be time dependent. See

Boltzmann, Wiss. Abh. II, p.83

Since such solutions are not well known, allow me to mention one of them. Consider the case of a harmonic attractive force so that $\vec{a} = \omega^2 \vec{r}$. Writing :

$$\log f = -h v^2 + \vec{k} \cdot \vec{v} + n$$

$$\left[h = \frac{\beta m}{2}; \quad \vec{k} = \beta m \vec{v}_0; \quad n = \log A - \frac{\beta m}{2} v_0^2 \right].$$

One gets from (5) :

$$\left. \begin{aligned} \frac{\partial n}{\partial t} - \omega^2 \chi_\alpha \kappa_\alpha &= 0 & (a) \\ \frac{\partial \kappa_i}{\partial t} + \frac{\partial n}{\partial x_i} + 2 \omega^2 x_{,i} &= 0 & (b) \\ \frac{1}{2} \left(\frac{\partial \kappa_i}{\partial x_j} + \frac{\partial \kappa_j}{\partial x_i} \right) - \delta_{ij} \frac{\partial h}{\partial t} &= 0 & (c) \\ \frac{\partial h}{\partial x_i} &= 0 & (d) \end{aligned} \right\} \quad (6)$$

So h is a function of t alone, and :

$$\vec{\kappa} = [\vec{\Omega} \times \vec{r}] + c \vec{r} + \vec{d}; \quad \frac{dh}{dt} = +c; \quad (7)$$

the motion is combination of rotation, radial expansion, and translation; Ω, c, d can still be functions of t . Eq (7) is still general, independently of outside forces. From (6a), (6b), one gets : $\dot{\Omega} = \text{const.}$ and

$$\ddot{d}_i + \omega^2 d_i = 0, \quad \ddot{c} + 4 \omega^2 c = 0$$

by eliminating n . Take for example the case :

$$\vec{d} = 0 \quad c = c_0 \cos 2\omega t$$

This gives :

$$h = h_0 + \frac{c_0}{2\omega} \sin 2\omega t,$$

and then :

$$n = -\omega^2 h_0 r^2 + \frac{\omega c_0 r^2}{2} \sin 2\omega t.$$

If h_0 is large enough, one gets a Gaussian density distribution with a curious "breathing" motion, accompanied by periodic temperature changes. In addition there can be rotations and translatory motions in which the center of the Gaussian gas cloud oscillates around the origin.

Already for an anisotropic harmonic potential $V = \frac{1}{2} \omega_1^2 X_1^2 + \frac{1}{2} \omega_2^2 X_2^2 + \dots$. One proves from eqs.(6) that h is constant in time, and \vec{r} and \vec{c} are zero. Oscillatory solutions are still possible. They will disappear if anharmonic terms are added.

The reason for the curious solutions is clearly the isochronic property of harmonic forces, which prevent them from producing the proper mixing.

3) Excursion on the linearized Boltzmann equation.

Since the H-theorem does not tell us the approach to equilibrium in detail, and also to show the different nature of the approach to equilibrium in the velocity and the space coordinates, it is good to look at the case in which the disturbance from equilibrium is small. Putting :

$$f = f_0 \left\{ 1 + h(\vec{r}, \vec{v}, t) \right\} \quad (8)$$

one gets the linear problem :

$$\begin{aligned} \frac{\partial h}{\partial t} &= -\vec{v} \cdot \nabla_r h - \vec{a} \cdot \nabla_v h + \int d\vec{v}_1 \int d\Omega g I(g, \theta) f_0 f_1 (h + h_1 - h - h_1) \\ &= S(h) + C(h) \end{aligned} \quad (9)$$

Consider first the case of no outside forces, and a disturbance dependent on \vec{r} and t alone. $f_0 = A e^{-\frac{\beta m}{2} v^2}$

; $C(h)$ is an isotropic operator, in fact one can show that it has the form ;

$$C(h) = -\sigma(v) h + \int d\vec{v}_1 K(v, v_1, \cos \phi) h(\vec{v}_1)$$

As a result the eigenfunctions of C , defined by

$$C(\Psi) = \lambda \Psi, \quad (10)$$

must have the form :

$$\Psi_{r\ell} = f_{r\ell}(v) Y_{\ell m}(\theta, \phi),$$

using polar coordination in vel. space. The eigenvalues $\lambda_{r\ell}$ are at least $2\ell + 1$ fold degenerate. There are 5 zero eigenvalues λ_{00} , λ_{20} , and λ_{40} corresponding to the eigenfunctions $1, v_x, v_x^2 \pm 3v_y^2$ and $v^2 - \frac{3}{2} v^2$, which are orthogonal. This is a consequence of the five conservation theorem.

All other eigen values are negative. Proof :

$$\lambda_{r\ell} = \frac{\int d\vec{v} f_0 \Psi_{r\ell} C(\Psi_{r\ell})}{\int d\vec{v} f_0 \Psi_{r\ell}^2} \quad (11)$$

$$\text{Numerator is } \int d\vec{v}_1 d\vec{v}_2 \int d\Omega g I(g, \theta) f_0 f_0 (\Psi' + \Psi'_1 - \Psi - \Psi_1)^6 - \frac{1}{4} \int d\vec{v} \int d\vec{v}_1 \int d\Omega g I(g, \theta) f_0 f_0 (\Psi' + \Psi'_1 - \Psi - \Psi_1)^2 < 0$$

using the same trick as used in the H-theorem. This shows that the disturbance decays monotonically to zero; the λ_{re} are the decay constants of the different modes. Developing :

$$h(\vec{v}, t) = \sum a_{re}(t) \Psi_{re}(t)$$

one gets

$$a_{re} = \lambda_{re} a_{re}$$

For Maxwell molecules, $g I(g, \theta)$ is independent of g , and since the transformation of the velocities in a collision is linear, it is clear that if h is a homogeneous polynomial in v_x, v_y, v_z , then $C(h)$ must also be a homogeneous polynomial of the same degree. So it should be possible to find the eigen-polynomials, which turn out to be the Sonine polynomials in C^2 , so :

$$\Psi_{re} \sim \int_{r+\frac{1}{2}}^{\infty} (c^2)^r \cdot c^2 Y_{lm}(\theta, \phi) \quad (12)$$

$S^{(m)}(x)$ is the coefficient of Z^m in $(1-Z)^{-n-1} e^{-\frac{x-Z}{1-Z}}$, and the corresponding eigenvalues are :

$$\lambda_{re} = 2\pi \int_0^\pi d\theta \sin^3 \theta F(\theta) \left[\cos^{2r+l} \frac{\theta}{2} P_l(\cos \frac{\theta}{2}) + \sin^{2r+l} \frac{\theta}{2} P_l(\sin \frac{\theta}{2}) - (1 + \delta_{r0} \delta_{l0}) \right] \quad (13)$$

They form a discrete set going to $-\infty$. Note that in (12) and (13) all velocities are measured in units of $\sqrt{2kT/m}$ and the collision operator is defined with the dimensionless $F(\theta)$. As a result, the times are measured in units $\frac{1}{n} \sqrt{\frac{m}{2k}}$ and since the cross sections are now $(x = \kappa)$

$\sim \sqrt{\frac{kT}{m}} \cdot \frac{1}{n} \sqrt{\frac{m}{2k}} = \sqrt{\frac{x}{kT}}$, the time unit is $\frac{1}{n\sigma} \sqrt{\frac{m}{2kT}}$, which is of the order of the time between collisions. The first negative eigenvalue

$$\lambda_{2,0} = \lambda_{1,0} = v_1 \sqrt{\frac{2k}{m}} \cdot \frac{1}{2} \int_0^\pi d\theta \sin^3 \theta F(\theta) \quad (14)$$

is the relaxation time of the gas already computed by Maxwell.

Whether for other force laws the eigen-value spectrum has the same character is not known but it is likely. However the approach of $\lambda \propto \omega$ is probably due to the infinite range of the x/r^5 force and the corresponding infinite value of the total cross section. I expect, say for elastic spheres, a finite lower bound, but I can't prove it.

Turning now to the streaming operator $S(h)$, clearly the eigen-values will in general not be real since $S(h)$ is not self adjoint. In fact for the harmonic force one can write :

$$\left[\left(v_x \frac{\partial}{\partial (v_x)} - \omega x \frac{\partial}{\partial v_x} \right) + \dots \right] h = \frac{\lambda}{\omega} h \tag{15}$$

At the left are three rotation operators in the (v_x, x) , (v_y, y) and (v_z, z) so clearly :

$$\lambda^{st.} = i (m_1 + m_2 + m_3) \omega \tag{16}$$

so that they are pure imaginary.

For Maxwell molecules it may be possible to determine the combined eigen functions and eigen-values of $S(h) + C(h)$, since polynomials in r and v remain polynomials in r and v of the same degree.

The main qualitative point to remember is, that the approach in velocity and in space are quite different. The approach to the local Maxwell distribution is monotonic and quite fast (time of order of time between collisions) while in space the approach will usually have a damped periodic character (depending on outside forces) and goes slowly.

4. The criticism of the kinetic method and the answer of Boltzmann.

The criticism is directed toward the H-theorem, and is an expression of the feeling of discomfort that somehow, using reversible mechanical models, Boltzmann succeeded in showing that H decreases monotonically till the equilibrium state is reached, that is, a typical irreversible behavior. These criticisms have been crystallized in two famous objections, the Umkehr-eindwand of Loschmidt and the Wiederkehr-eindwand of Zermelo. Especially the latter, based on theorem of Poincaré which says that a bounded mechanical system is always quasi-periodic,

seems decisive. On the energy surface the point in phase space represents the state of the gas will return after the Poincaré cycle to any surrounding of the initial position. The H must therefore sometime increase.



Boltzmann's answer was not well understood in his time, probably because of his rather uncritical use of probabilistic terms. It

amounts to this : note that a distribution in phase-space of a finite number of molecules required finite cells w_1, w_2, \dots . The number in cell w_i

$$m_i = f_i \omega_i \rightarrow f(r, p, t) d\vec{r} d\vec{p}$$

must be appreciable. With a distribution Z in \mathcal{M} -space corresponds in Γ -space a whole volume (3 N-dim.)

$$W(Z) = \frac{N!}{m_1! m_2! \dots} \omega_1^{n_1} \omega_2^{n_2} \dots \quad (17)$$

Now one proves that with the accessory conditions

$$\sum n_i = N \quad \sum \epsilon_i n_i = E$$

the M.B. distribution $\bar{n}_i = A \omega_i e^{-\beta \epsilon_i}$

overwhelmingly maximizes $W(Z)$. If one therefore assumes that there is no priori preference for the motion of the Γ -point for any portion of the energy surface, then one can conclude that :

1. If the gas is not in the M.B. distribution it almost always will go into it.
2. Once it has the M.B. distribution it almost always will stay there.

Clearly in this way there is no conflict with the Poincaré theorem. The further development of this statistical method of Boltzmann, leads to a completely satisfactory description of the equilibrium properties in the first place of gases, and then by considering more complicated systems as a large molecule to the prescription for the calculation of all thermodynamic properties from the partition function of the system.

However, the details of the approach to the equilibrium state are lost. The relation to the kinetic method is dark, and there is therefore no general method for complicated systems (say dense gases for instance) to derive the non-equilibrium properties from the molecular picture.

5. Excursion on stochastic processes.

The whole situation has been further clarified by an example of Ehrenfest and by the work of Smoluchowski on the concentration fluctuation of colloidal suspensions.

The example of Ehrenfest : Consider two urns A and B, containing

N_A and N_B balls respectively. Suppose

$$N_A + N_B = 2R$$

$$N_A - N_B = 2K$$



At fixed intervals a ball is chosen at random from among the $N_A + N_B$ and moved from its urn to the other. This is a kind of model for temperature or concentration equalization between two reservoirs. It is also interpretable as a random walk problem with attracting center. Most complete discussion :

M. Kac : Amer. Math. M. 54, 369, 1947.

Analogue to Boltzmann statistical method :

$$W(K) = \frac{2^R R!}{N_A! N_B!} \left(\frac{1}{2}\right)^{2R} \quad (18)$$

Most probable state (= Equilibrium state) $N_A = N_B$ or $k = 0$ and this is very sharp if R is large. In fact, then :

$$W(K) = \frac{1}{\sqrt{\pi R}} e^{-\frac{k^2}{R}}$$

One can now go farther, because there is a "probability mechanism" which allows one to describe how k changes; the different k -values form a discrete random series.

Analogous is the situation in the concentration fluctuations :



Smoluchowski, Phys. ES..17, 557-585 (1916)

$$W(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n} \quad \text{with } p = \frac{v}{V}$$

Equilibrium state $n = N \frac{v}{V}$. Transition by the "mechanism" of a jumping chance.

Clearly the k or n correspond to the distribution (n_1, n_2, \dots) for the gas, and the behavior of k is just like the behavior according to Boltzmann of the state of the gas. Any value of k between $-R$ to R will occur, but of course extremely rarely (and the Poincaré cycle is correspondingly long) if k is far from equilibrium. And there is no distinction between the future and the past. Irreversibility is a human illusion, or as Smoluchowski expresses it :

A process will be considered either irreversible or reversible according to whether the initial state has a recurrence time (Poincaré cycle) which is long or short compared to the time of observation. And

one should say in addition, that there is such a sharp variation of the length of the recurrence time (due to the large number of molecules) with the degree of deviation from equilibrium that the two alternatives are almost a discontinuous function of the deviation.

6. Discrete Markoff series.

Of course if one knows the "probability mechanism" one can go further, as I said before, and one can get some idea of how fast the equilibrium state is reached. The situation is especially simple for the so-called Markoff processes, of which the Ehrenfest model (but not the concentration fluctuation) is an example.

In general, one describes a random series $k_1, k_2 \dots$ by the set of distribution functions :

$$W_1(k) = \text{probability of finding } k$$

$$W_2(k_1, k_2; s) = \text{probability of finding a pair } k_1, k_2$$

s steps apart; etc.

A Markoff series is the next simplest to the purely random series (where all k's are independent of each other, so that $W_1(k)$ gives all the information). In a Markoff series all information is contained in the second distribution function which of course implies the first. One can also say that the probability of finding a value k depends only on the previous value of k. Introducing the conditional probability distribution $P(n/m, s)$, the probability of finding m after s steps starting with n, one has for a Markoff series :

$$P(n/m, s) = \sum_k P(n|k, s-1) P(k|m, 1) \quad (19)$$

Call $P(k/m, 1) = Q(k, m)$; then since $\sum_k Q(k, m) = 1$, one can write (19) in the form (suppressing n) :

$$P(m, s) = \sum_k P(k, s-1) Q(k, m)$$

$$= \sum_k P(k, s-1) Q(k, m) + P(m, s-1) \left[1 - \sum_k Q(k, m) \right]$$

or

$$P(m, s) - P(m, s-1) = \sum_k P(k, s-1) [Q(k, m) - P(m, s-1) Q(k, m)] \quad (20)$$

This smells like the Boltzmann equation; the rate of change of P with "time" (= s) is equal to the gains due to transitions from k to m minus the losses due to transitions from m to any value different from m. However, note that the variable m corresponds in the gas case to the

set of numbers $(n_1, n_2 \dots)$. It is therefore really an equation on a higher level than the Boltzmann equation (which tells how each n_1 changes because of the collisions). Equation (20) really corresponds to a kind of "master equation" which would have to tell how the probability of a distribution $(n_1, n_2 \dots)$ changes with time. Note also that (20) is a linear equation. In equation (20) one has to suppose that $Q(k, m)$ is known. It describes the basic "probability mechanism". One then has to solve Equation (20) for $P(m, s)$ assuming an "initial" condition, say $P(m, 0) = \delta(m, n)$.

For the Ehrenfest model in each step the k can only change with one, and

$$Q(k_0, k) = \frac{R + k_0}{2R} S(k_0 - 1, k) + \frac{R - k_0}{2R} S(k_0 + 1, k) \quad (21)$$

so that (19) becomes

$$P(m, s) = \frac{R + m + 1}{2R} P(m + 1, s - 1) + \frac{R - m + 1}{2R} P(m - 1, s - 1) \quad (22)$$

One proves easily that

$$\langle m(s) \rangle = \sum_m m P(m, s) = \left(1 - \frac{1}{R}\right) \langle m(s-1) \rangle$$

so that if initially one is sure that $m = n$:

$$\langle m(s) \rangle = n \left(1 - \frac{1}{R}\right)^s$$

This exponential approach of the average value from n to the equilibrium value zero is the analogue of the monotonic approach of any velocity distribution to the Maxwell distribution. One can now of course also calculate the square average and show :

$$\langle m^2(s) \rangle = n^2 \left(1 - \frac{2}{R}\right)^s + \frac{1}{2} R \left[1 - \left(1 - \frac{2}{R}\right)^s\right]$$

so that for $s \rightarrow \infty$, $\langle m^2(s) \rangle \rightarrow \frac{R}{2}$ which is the value which follows from $W_1(m)$. In fact, one can show that any distribution $P(m, s)$ approaches for $s \rightarrow \infty$ the first probability distribution $W_1(m)$ monotonically. In general, the proof goes as follows : from the basic equation :

$$P(n | m, s) = \sum_k P(n | k, s-1) Q(k, m)$$

one sees that one gets $P(n / m, s)$ by successive matrix multiplication of

$Q(k, m)$, which fulfills the conditions :

$$Q(k, m) \geq C \quad \sum_m Q(k, m) = 1$$

It is obvious to introduce the eigenvalues of $Q(k, m)$. Note, however, that $Q(k, m)$ is not symmetric, so one must consider the linear equations:

$$\lambda x_k = \sum_s Q_{sk} x_s$$

together with the adjoint equations :

$$\lambda y_h = \sum_t Q_{ht} y_t$$

(24)

The secular determinant

$$\| \lambda_{sk} - Q_{sk} \| = 0$$

(25)

leads to the eigenvalue λ_i , and to λ_i corresponds

$$\lambda_i \rightarrow \begin{cases} x_{ik} & k = 1, 2, \dots \\ y_{ih} & h = 1, 2, \dots \end{cases}$$

and one has the two orthogonality and normalization relations :

$$\sum_k x_{ik} y_{kj} = \delta_{ij} \quad \sum_s y_{is} x_{sj} = \delta_{ij}$$

By adding all columns to the first, one sees that $\lambda = 1$ is an eigenvalue; call it λ_1 , then from (24) one verifies that

$$x_{1k} = W_i(k); \quad y_{1h} = 1$$

One can prove further that all other eigenvalues are in absolute value less than one; in fact, for the Ehrenfest model Kac has proved that

$\lambda_i = \frac{i}{R}$, $-R \leq i \leq R$, and he has determined also all the eigenvectors:

$$x_{ik} = C \binom{i}{k+R} \quad y_{ih} = \frac{(-1)^{R+h}}{2^{i+R}} \binom{-R}{i+R}$$

where the symbol C_m^n is defined by :

$$(1 - Z)^{R-n} (1 + Z)^{R+n} = \sum_{m=0}^{2R} C_m^n Z^m$$

From the orthogonality relations follows then in the standard way :

$$Q_{X_m} = \sum_j \lambda_j y_{nj} X_{jm}$$

$$P(n | m, s) = \sum_j \lambda_j^s y_{nj} X_{jm} \tag{26}$$

$$= W_1(m) + \sum_{j>1} \lambda_j^s y_{nj} X_{jm}$$

so that for $s \rightarrow \infty$ $P(n | m, s) \rightarrow W_1(m)$.

7. The mean recurrence time.

One can give now also further details about the recurrence and persistence time. Basic paper is

Smoluchowski, Wiener Ber. 124, 339, 1915.

For Markoff processes everything can be done very elegantly. Define :

$P'(n | n, s)$ = probability, given n , that after s steps n occurs for the first time

Then clearly :

$$P(n | n, s) = P'(n | n, s) + \sum_{k=1}^{s-1} P'(n | n, k) P(n | n, s-k) \tag{27}$$

Introduce now the generating functions :

$$h(n | n, Z) = \sum_{s=1}^{\infty} P(n | n, s) Z^s$$

$$g(n | n, Z) = \sum_{s=1}^{\infty} P'(n | n, s) Z^s$$

Then from (27) :

$$g(n | n, Z) = h(n | n, Z) = \sum_{s=1}^{\infty} \sum_{k=1}^{s-1} Z^s P'(n | n, k) P(n | n, s-k)$$

In double sum, interchange and call $s-k = r$:

$$\sum_{s=1}^{\infty} \sum_{k=1}^{s-1} = \sum_{k=1}^{\infty} \sum_{s=k+1}^{\infty} = \sum_{k=1}^{\infty} \sum_{r=1}^{\infty}$$

so it becomes :

$$\sum_{k=1}^{\infty} P'(n/n, k) Z^k \sum_{r=1}^{\infty} P(n/n, r) Z^r = g(n/n, Z) h(n/n, Z)$$

and therefore :

$$\begin{aligned} g(n/n, z) &= \frac{h(n/n, z)}{(1+h(n/n, z))} \\ &= 1 - \frac{1}{1+h(n/n, z)} \end{aligned} \tag{28}$$

Using now the form (26) for $P(n/n, z)$, then clearly :

$$1+h(n/n, z) = \frac{W_1(n)}{1-z} + p(z)$$

where $p(z)$ is regular around $z = 1$, due to the fact that all eigenvalues λ are < 1 , except λ_1 . From (28) one thus sees that

$$\lim_{z \rightarrow 1} g(n/n, z) = \sum_{s=1}^{\infty} P'(n/n, s) = 1$$

$P'(n/n, s)$ is therefore a bona fide probability. Further :

$$\frac{dg}{dz} = \frac{\frac{dh}{dz}}{(1+h)^2} = \frac{\frac{W_1(n)}{(1-z)^2} + p'(z)}{\left[\frac{W_1(n)}{1-z} + p(z) \right]^2}$$

so that :

$$\lim_{z \rightarrow 1} \frac{dg}{dz} = \frac{1}{W_1(n)}$$

This gives the mean recurrence time $\bar{T}(n)$, since

$$\bar{T}(n) = \tau \sum_{j=1}^{\infty} j P'(n|n, j) = \tau \lim_{z \rightarrow 1} \frac{d g}{d z} = \frac{\tau}{W_1(n)} \quad (29)$$

The mean square recurrence time depends already on all the eigenvalues and can therefore only be calculated for special models like the Ehrenfest model.

The concentration fluctuations of a colloidal suspensions as analysed by Smoluchowski do not form a Markoff process. However, the result (29) (with appropriate definition of $\bar{T}(n)$) is still valid. It is interesting to see how it compares with experiment (Svedberg). In these experiments $\tau = 1/33$ min.; the average number $\langle n \rangle = \checkmark = 1.55$; the first probability distribution $W_1(n) \approx \frac{e^{-\checkmark} \checkmark^n}{n!}$ (Poisson)

n	\bar{T}_{obs}	\bar{T}_{calc}
0	6.08	5.54
1	3.13	3.16
2	4.11	4.05
3	7.85	8.07
4	18.6	20.9

The check is therefore pretty good. The value $n = 7$ was observed only once; $\bar{T}(7)$ would be $1105 \tau = 27$ min., while the whole series of observations was about 600. For $n = 17$, $\bar{T} = 500,000$ years!, so the transitions from $n = 17$ would certainly be judged to be irreversible.

The Ideas of Gibbs

8. The notion of an ensemble.

In the Ehrenfest example I pointed out already that the random variable k corresponds in the case of the ideal gas to the whole distribution (n_1, n_2, \dots) in \mathcal{M} -space. To describe the change of k in the Ehrenfest model we introduced the probability distribution $P(k, t)$ of which we proved that it approached monotonically the "equilibrium" distribution $W_1(k) = \left(\frac{2R}{R-k}\right) \left(\frac{1}{2}\right)^{2R}$. In order therefore to describe in more detail how the Maxwell-Boltzmann distribution is reached for the gas, one must introduce the notion of the probability $P(n_1, n_2, \dots, t)$ of a certain state (n_1, n_2, \dots) ; or, using the description of the state of the gas by a point Q in \mathcal{F} -space, one must introduce a probability distribution $P(Q, t) = P(x_1 \dots x_N, t)$ in \mathcal{F} -space. (Notation: $x_i = (q_i, p_i)$ = coordinate and momentum of the i^{th} particle. This can only mean that one considers not only the given system but a large number of copies of it; an ensemble, in the language of Gibbs.

Similarly, in the Ehrenfest model, to test the result (say, of Z) for $P(k_0/k, t)$, one must consider an ensemble of experiments. In each the initial distribution is determined by k_0 , but the successive values would be different and one would obtain Z sequences of k -values, from which at any time the distribution $P(k_0/k, t)$ can be found. Analogously, if one starts with a distribution (n_1, n_2, \dots) , corresponding to a region on the energy surface in the \mathcal{F} -space of the gas, the different members of the ensemble (represented by points in this region) would move quite differently and provide different series of successive states; or, in the language of Gibbs, one has a streaming of the ensemble "fluid" over the energy surface. Of course there is also an essential difference; in the Ehrenfest model the "probability mechanism" is known, while in the case of the gas the motion of the point in \mathcal{F} -space is in principle completely determined by the laws of mechanics and the differences in behavior are due to the different initial positions on which the motion depends very sensitively because of the sharp short-range interactions between the molecules.

In the Ehrenfest model $P(k_0/k, t)$ approaches $W_1(k)$. If one expresses the basic idea of the statistical method of Boltzmann for the gas, now, by saying that the a priori probability of some state of the gas is determined by the volume in \mathcal{F} -space to which the state corresponds, then one can expect that the $P(n_1, n_2, \dots; t)$ will, for $t \rightarrow \infty$, monotonically approach

$$\frac{N!}{n_1! n_2!} \left(\frac{\Omega_1}{\Omega}\right)^{n_1} \left(\frac{\Omega_2}{\Omega}\right)^{n_2}$$

(where Ω is the volume of the whole phase (\mathcal{M})space), so that the overwhelming majority of the members of the ensemble will have a Maxwell Boltzmann distribution. Or, in the language of Gibbs, one can expect

that any initial density distribution of the ensemble over the energy surface (which for an ideal gas is of course the hypersphere

$$\sum \frac{P_m}{\Omega_m} = E \quad \text{will approach the uniform distribution (i.e.,}$$

uniform between the surfaces E and $E + dE$), or, as Gibbs call it, the micro-canonical distribution. That the volume in phase space, or the "statistical factor" in the problem of partition of the energy E between N independent particles leads for large N to the Maxwell Boltzmann distribution is perhaps not quite familiar (although given by Maxwell). The proof is as follows : since $p dp \sim \sqrt{\epsilon} d\epsilon$, the probability that one particle has energy between ϵ_1 and $\epsilon_1 + d\epsilon_1$ is :

$$f(\epsilon_1) d\epsilon_1 \sim d\epsilon_1 \sqrt{\epsilon_1} \dots d\epsilon_2 \dots d\epsilon_N \sqrt{\epsilon_2 \epsilon_3 \dots \epsilon_N}$$

where the integral is to be taken over all values so that

$$\epsilon_2 + \epsilon_3 + \dots + \epsilon_N = E - \epsilon_1 \quad \text{. By induction or otherwise one gets (dropping index 1) :}$$

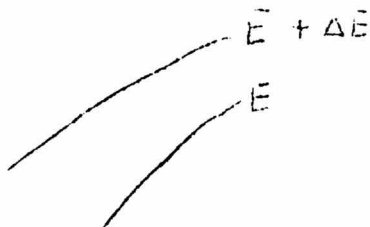
$$f(\epsilon) d\epsilon = A_N \sqrt{\epsilon} (E - \epsilon)^{\frac{3N-3}{2}} d\epsilon$$

where A_N is a normalization factor. This gives $\bar{\epsilon} = E/N$ (Maxwell's proof of equipartition), and it is easy to prove that for large N :

$$f(\epsilon) d\epsilon = A \sqrt{\epsilon} e^{-\frac{3\epsilon}{2E}} d\epsilon$$

the Maxwell-Boltzmann distribution.

Of course one now can generalize to more complicated systems than ideal gases, and in fact Gibbs introduced the microcanonical ensemble (now better defined as the uniform distribution between two neighboring energy surfaces E and $E + \Delta E$ in the Γ -space :



- Note that these surfaces need not be parallel). immediately for general systems. It was one of his aims to give a more deductive and lucid presentation of the methods of Boltzmann, and in this he

certainly succeeded! I will not discuss the further developments, such as the other special ensembles (canonical, grand ensemble, the string of theorems connecting them with each other, the thermodynamic analogies etc.). They lead again to the basic relation between the free energy of

the system and the partition function, which gives in principle the solution of all the problems of statistical physics (connection between macroscopic properties and the molecular structure and interactions) for systems in thermodynamic equilibrium.

It should be emphasized that, while in the Ehrenfest model the equal a priori probability of the two boxes (from which $W_1(k)$ follows) is put into the problem, for the gas the assumption of Boltzmann must be considered to be a property of the mechanical system. One calls it the ergodic property. What it implies for the mechanical motion can be explained as follows: in the Ehrenfest model, clearly the different series of k -values of the ensemble can also be considered as successive large chunks of a very long single series in time; therefore for any quantity the time average will be the same as the ensemble average, and the same must be assumed for the gas. That is,

$$\langle f(x_1, \dots, x_N) \rangle_{\text{time}} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T f(x_1(t), \dots, x_N(t)) dt$$

$$= \int \dots \int dx_1 \dots dx_N \rho(E) \langle f(x_1, \dots, x_N) \rangle_{\text{ensemble}}$$

where $\rho(E)$ is the microcanonical probability distribution. This property, although very plausible because of the erratic motion of the Γ -point, is of course not proved. It can be reduced to the assumption of metrical transitivity (from which the ergodic property then follows) but although an advance, it does not help the physicist!

9. The approach to the microcanonical distribution and the Gibbs H-theorem.

See Gibbs, Chapter 12.

As I said, it is very plausible that any distribution of the ensemble "fluid" between the energy surfaces E and $E + \Delta E$, will monotonically become the uniform or microcanonical distribution. It is appropriate here to make some comments on the question of the approach.

a) First, the monotonic approach is not in conflict with the Poincaré theorem. Each member of the ensemble has a quasi periodic motion, and one can prove (see M. Kac, Bull. Amer. Math. Soc. 53, 1002, 1947) that for intermittent observation and for a metrical transitive mechanical system the average recurrence time (or Poincaré cycle) is $\sim \frac{1}{\Delta E}$ (where ΔE is the area on the energy surface), quite analogous to the result $\bar{T} = \frac{1}{W_1(n)}$ for the Ehrenfest model.

b) It is not true that the uniform distribution is the only stationary distribution. To find the most general stationary distribution I have to remind you of a general characteristic of the streaming, expressed by the Liouville theorem : the streaming of the "ensemble fluid" is like that of an incompressible fluid. The proof is so simple that I shall give it :

Proof : The "velocity" \vec{V} (with components $\dot{q}_1 \dots \dot{p}_N$) fulfills the condition :

$$\text{Div } \vec{V} = \sum_i \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = \sum_i \left(\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} \right) \equiv 0$$

by virtue of Hamilton's equations. Since one always has the continuity equation :

$$\frac{D\rho}{Dt} + \rho \text{div } \vec{V} = 0$$

one has therefore :

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + \sum_i \left(\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right) = 0$$

i.e. :

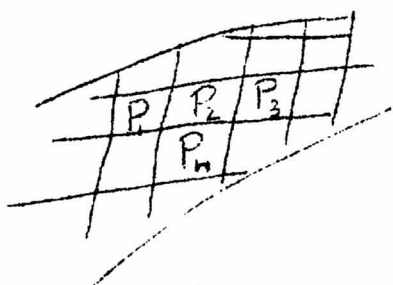
$$\frac{\partial \rho}{\partial t} = \{ H, \rho \}$$

(1)

(the Poisson bracket of H and ρ).

The most general stationary density distribution is therefore a distribution where ρ is constant along stream lines (lines of constant H), but not necessarily the same constant along different stream lines.

c) Since ρ remains constant if one moves with the fluid, the distribution can only become uniform in a "coarse-grained" sense, as pointed out by Ehrenfest :



If the density initially is constant in different regions (say $P_1, P_2 \dots$), then because of the distortion due to the streaming the average density

$$\rho = \frac{\int \dots \int \rho dx_1 \dots dx_N}{\Delta x_1 \dots \Delta x_N}$$

over the fixed regions will become equal. This can be shown analytically

by the Gibbs H-theorem.

We define this H-function by :

$$\begin{aligned}
 H_G &\equiv \sum_m P_m \log P_m (\Delta x_1, \dots, \Delta x_N)_m = \int \dots \int dx_1 \dots dx_N P \log P \\
 &= \int \dots \int dx_1 \dots dx_N P \log P \\
 &\quad \delta \tau_m = (\Delta x_1, \dots, \Delta x_N)_m
 \end{aligned} \tag{2}$$

is the volume of the m^{th} cell.

Now start with a non-uniform ensemble, in which the density is actually constant in the set of regions $\delta \tau_1, \delta \tau_2 \dots$. So at $t = 0$, the fine-grained and coarse-grained densities are identical and

$$H = H_0 = \int P_0 \log P_0 dx_1 \dots dx_N$$

Now consider at a later time t :

$$\begin{aligned}
 H - H_t &= \int \dots \int (P_0 \log P_0 - P_t \log P_t) dx_1 \dots dx_N \\
 &= \int \dots \int (P_t \log P_0 - P_t \log P_t - P_t + P_t) dx_1 \dots dx_N,
 \end{aligned}$$

where we have used $\int \dots \int P_t dx_1 \dots dx_N = \int \dots \int P_0 dx_1 \dots dx_N = 1$

by normalization and :

$$\int \dots \int P_t \log P_t dx_1 \dots dx_N = \int \dots \int P_0 \log P_0 dx_1 \dots dx_N$$

because of Liouville.

Using the lemma that $F(x, y) = x \log x - x \log y - x + y \geq 0$ (zero only for $x = y$), one sees that

$$H_0 - H_t \geq 0$$

and that H_G is smallest for the coarsely uniform ensemble.

10. - Criticism of the Gibbs Theorem.

Ehrenfest¹ expressed the opinion that the time for the approach to the uniform distribution may well be several Poincaré cycles. If so, it clearly would have nothing to do with the actual approach to equilibrium. I must confess that this is one of the few points I do not understand in the Encyclopedia article. I think the time of approach has nothing to do with the Poincaré cycle. It will, rather, depend on the size of the coarse-grained cells; the larger they are chosen the sooner they will become roughly uniform.

In my opinion the important objection is that the theorem has little to do with real irreversible processes since it does not tell which coarse-grained density "corresponds to our knowledge" of a certain initial non-equilibrium situation. Of course this is connected with the difficulty of using an ensemble for the description of a single system. The justification must lie in the fact that a macroscopic description of a system is so rough that a very large number of microscopically different states of the system correspond to it. One must then assume that the actually observed macroscopic changes of state are the same for the overwhelming majority of the ensemble, so that the average of some quantity over the (non-stationary) ensemble as a function of time will represent the change of the quantity with time for the single system.

The trouble is, not only that such statements are hard to prove, but there is no hint or guess on how to construct such non-equilibrium ensembles. As a result there is no general theory for non-equilibrium phenomena in Gibb's scheme. Of course, in view of the enormous variety of characteristic times involved (especially if solids are present), such a general theory is probably too much to ask for. However it should be possible, say for dense gases, to show how in principle typical transport quantities (like for instance, the heat conductivity) are related to the intermolecular forces.

11. - "Rückblick" on the kinetic method of Boltzmann.²

In particular for nearly ideal gases one would like to know how the ... "Stoszzahl Ansatz" and the Boltzmann equation discussed in the first lecture fit into the general scheme of Gibbs.

A rather obvious idea is to interpret the Stoszzahl Ansatz as an assumption for the transition probability between the different states (n_1, n_2) of the ideal gas. I proposed to do this in some analogous statistical problem in the theory of cosmic ray showers (Physica, 7, 344, 1940; Phys. Rev. 62, 497, 1942), and it was then taken up by Siegert (Phys. Rev. 76, 1708, 1949) and recently much further developed by M. Kac.

1. Enziyclopedia, P.61

2. Footnoté on next page.

Let $n_1, n_2 \dots$ be the number of molecules in the different velocity-cells $\omega_1, \omega_2 \dots$. Assume the distribution in space to be uniform, and no outside forces. Let the probability per unit time of a collision $(i, j) \rightarrow (k, l)$ be: $a_{ij}^{kl} n_i n_j$; then it follows that the probability distribution $P(n_1, n_2 \dots; t)$, which, recall, is analogous to $P(k, t)$ in the Ehrenfest model, will satisfy the "master equation": (Analogous to the Smoluchowski equation for the Ehrenfest case (20) p.10)

$$\frac{\partial P(n_1, n_2 \dots, t)}{\partial t} = \frac{1}{2} \sum_{(ij)(kl)} \left[a_{ij}^{kl} (n_k + 1)(n_l + 1) P(n_1, \dots, n_k + 1, n_l + 1, \dots, n_i - 1, n_j - 1, \dots, t) - a_{ij}^{kl} n_i n_j P(n_1, n_2 \dots, t) \right] \quad (1)$$

Note that this is a linear equation that is given by the Stosszahl Ansatz assumption. By summing over all values of $n_1, n_2 \dots$ with the condition $\sum n_i = N$, and assuming microscopic reversibility: $a_{ij}^{kl} = a_{kl}^{ij}$, and noting the symmetry in (ij) et (kl) ; furthermore $a_{ij}^{kl} = 0$ and in (1) $i, j \neq k, l$, one sees that

$$\frac{d}{dt} S' P(n_1, n_2, \dots, t) = 0 \quad (2)$$

(where S' means that one is to sum over all $n_1, n_2 \dots$ subject to $\sum n_i = N$) so that the normalization $S' P(n_1, n_2 \dots; t) = 1$ is conserved. For the rate of change of the average number $\bar{n}_s = S' n_s P(n_1, n_2 \dots; t)$ in cell ω_s one then finds:

$$\frac{d\bar{n}_s}{dt} = \frac{1}{2} \sum_{jkl} a_{ij}^{kl} S' \left[n_s (n_k + 1)(n_l + 1) P(\dots, n_k + 1, n_l + 1, \dots, n_i - 1, n_j - 1, \dots) - n_s n_i n_j P(n_1, n_2, \dots) \right]$$

One must distinguish in the "straight" sum the cases where s is different from i, j, k, l (which are all different from each other) and where it is equal to any one of the i, j, k, l . Changing the summations in the first "round" sum back to n_k, n_l, n_i, n_j , one then easily finds that the third

²(Foot-note from page 21). This contrasts strongly with the kinetic method of Boltzmann, where the approach to equilibrium can be found in detail, since the process is probabilistic, rather than dynamical. The natural question then is: Can we "fix up" Boltzmann's method now that we have more insight into the nature of the difficulties? Gibbs, in his famous chapter 12, tells us nothing on this point.

order terms in the n's always cancel, and one gets :

$$\frac{dn_i}{dt} = \sum_{j,k} a_{ij}^k (n_k n_j - n_i n_{k+j}) \quad (3)$$

This would be just the Boltzmann equation if one could put $\overline{n_k n_l} = \overline{n_k} \overline{n_l}$ and $\overline{n_s n_j} = \overline{n_s} \overline{n_j}$ that is, if one could neglect the correlations, which presumably would be permissible if all the occupation numbers are large.

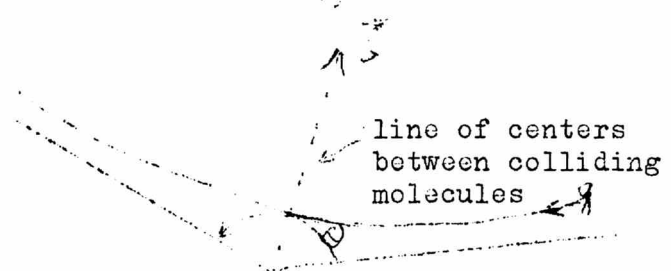
Siegert has shown that (1) leads, for $t \rightarrow \infty$, to the equilibrium distribution $\frac{N!}{n_1! n_2! \dots} \left(\frac{e^{-\epsilon_i}}{Z}\right)^{n_i}$, just as we saw in the Ehrenfest example that $P(k, t)$ for $t \rightarrow \infty$ approaches the first probability distribution $W_1(k)$ which is proportional to $N! / N_A! N_B!$

12. - Formulation of the master equation on the energy surface.

It is nicer and more concrete to express the same idea in the "Gibbs" way. For the ideal gas, the energy surface is a $3N-1$ dimensional hyperspherical surface $v_1^2 + v_2^2 + \dots + v_{3N}^2 = 2mE$ imbedded in $3N$ -dimensional space. Assume that on the energy surface the P -point has a random walk motion where the probability of a step in time dt is again determined by the "Stoszzahl Ansatz". Since momentum is also conserved, one can put $\vec{v}_1 + \vec{v}_2 = \vec{v}_3 + \vec{v}_4 = 0$, so the motion is really on a $3N-3$ dimensional sphere (again only the velocity distribution will be considered).

Let $P(\vec{R}, t)$ be the probability that the P -point is at \vec{R} at time t , where $\vec{R} \equiv (v_1, v_2, \dots, v_{3N})$.

Consider a collision between molecules i and j . To represent it, we use a "collision operator" A . A collision is rotation of the vector define $A_{ij}(\vec{R}) \vec{R} = (\vec{v}_1, \vec{v}_2, \dots, \vec{v}_i - \vec{v}_j, \dots, \vec{v}_i + \vec{v}_j, \dots, \vec{v}_N)$



as the rotated vector; $\vec{q}_j = \frac{\vec{v}_i - \vec{v}_j}{|\vec{v}_i - \vec{v}_j|}$

\vec{e} unit vector in the perihelium direction. If total volume is V , then according to the Stoszzahl Ansatz, the problem per second of a specific collision is $\int \frac{d\Omega}{4\pi} g_{ij} I(g_{ij}, \theta)$ and one has therefore

$$\frac{\partial \phi(\vec{R}, t)}{\partial t} = \frac{1}{2V} \sum_{i,j} \int d\Omega g_{ij} I(g_{ij}, \theta) \{ \phi(A_{ij} \vec{R}, t) - \phi(\vec{R}, t) \} \quad (4)$$

Note again that this is a linear equation. Furthermore if the N particles are indistinguishable one should only allow symmetric functions $\phi(\vec{v}_1, \dots, \vec{v}_N, t)$

. By contraction (= integration over all v's except, say, v_1, \dots, v_k , where k is arbitrary) one gets the partial velocity distribution of groups of particles. In particular for

$$f^{(N)}(\vec{v}_1, t) \equiv \int \dots \int d\vec{v}_2 \dots d\vec{v}_N \phi(\vec{R}, t)$$

(in the integral, energy and momentum conditions must of course be taken into account) one gets the Boltzmann-like equation :

$$\frac{\partial f^{(N)}(\vec{v}_1, t)}{\partial t} = \frac{N-1}{V} \int d\vec{v}_2 \int d\Omega q I(q, \theta) \times \left\{ f^{(N)}(\vec{v}_1 - (\vec{q} \cdot \vec{S}) \vec{S}, \vec{v}_2 + (\vec{q} \cdot \vec{S}) \vec{S}) - F^{(N)}(\vec{v}_1, \vec{v}_2, t) \right\} \quad (5)$$

(We have chosen the subscript 2 for the collision "partner" of 1; of course it is arbitrary). In the proof one must distinguish again the cases $i, j \neq 1$ which give no contribution, and $i = 1, j \neq 1$; $i \neq 1, j = 1$, which give the two terms in (5). Eq. (5) would become the Boltzmann equation if one could assume

$$f_2^{(N)}(\vec{v}_1, \vec{v}_2) = F^{(N)}(\vec{v}) f_1^{(N)}(\vec{v}_2)$$

and if one could then introduce the average number of particles

$$f(\vec{v}, t) = \frac{N}{V} f_1^{(N)}(\vec{v}, t) \quad \text{instead of } f^{(N)}.$$

Again it can be expected that for large t the $\phi(\vec{R}, t)$ becomes the uniform distribution (microcanonical ensemble), which as we saw, leads for large N to the M.B. distribution for $f_1(\vec{v})$.

Marc Kac has been able to go further. To do this, he considered a simplified version of the basic equation (4); it is a kind of one-dimensional Maxwell model. Let $\vec{R} = x_1 x_2 \dots, x_N$ and

$$A_{ij}(\theta) \vec{R} = x_1, x_2, \dots, x_{i-1}, x_i (\cos \theta) + x_j \sin \theta, \dots, x_{i+1} \sin \theta + x_j (\cos \theta), \dots, x_N \\ = e^{i\theta L_{ij}} \vec{R}$$

where L_{ij} is the infinitesimal rotation operator in the ij plane. Assume that the probability for such a rotation depends only on θ . The random walk is executed on the sphere $x_1^2 + x_2^2 + \dots + x_N^2 = N$,

and the master equation then is :

$$\frac{\partial \phi(\vec{R}, t)}{\partial t} = \frac{V}{2N} \sum_{i,j} \int_{-\pi}^{\pi} d\theta \{ \phi(A_{ij}(\theta) \vec{R}, t) - \phi(\vec{R}, t) \} \quad (4a)$$

We can write (4a) as $\partial_t \phi = \Omega \phi$,

where

$$\Omega = \frac{v}{2N} \sum_{ij} (e^{i\theta L_{ij}} - 1).$$

The Boltzmann equation analogous to (4a) is :

$$\frac{\partial f(x,t)}{\partial t} = v \int_{-\infty}^{+\infty} dy \int_{-\pi}^{+\pi} F(\theta) d\theta \{ x \cos \theta + y \sin \theta, t \} f(-x \sin \theta + y \cos \theta, t) - f(x,t) + f(y,t) \}$$

The "collision cross section" will be $\int_{-\pi}^{+\pi} F(\theta) d\theta$, and we will assume it to be finite, and it is also appropriate to assume $F(\theta)$ an even function of θ .

FURTHER RESULTS OF KAC; THE BASIC QUESTION

13. - The Propagation of the "Boltzmann property".

Let $\phi_N(\vec{R}, 0)$ be a sequence of probability density functions, defined on the sphere $\sum_{i=1}^N X_i^2 = N$, which have the "Boltzmann property"

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln \phi_N(x_1, \dots, x_N, 0) = \sum_{j=1}^k \lim_{N \rightarrow \infty} f_j^{(N)}(x_j, 0). \quad (1)$$

Then Kac was able to prove that the sequence of functions $\phi_N(\vec{R}, t)$ which are the solutions of the master equations with $\phi_N(\vec{R}, 0)$ as initial values, also have the Boltzmann property, i.e. :

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln \phi_N(x_1, \dots, x_N, t) = \sum_{j=1}^k \lim_{N \rightarrow \infty} f_j^{(N)}(x_j, t). \quad (1 a)$$

This theorem, of which the proof is still rather complicated, is of interest because it elucidates what previously was hidden under the assumption of molecular chaos. Clearly $\phi_N(\vec{R}, t)$ contains in general much more information than $f_j(x, t)$. However one must expect that all correlations are "broken" very quickly, and the state of molecular chaos (for which the Boltzmann property holds) is established and then persists (in time). The non-linearity of the Boltzmann equation is from this point of view, due only to the special initial distribution; the basic problem (= the initial value problem for the master equation) is a linear problem.

14. - The approach to the uniform distribution.

It is again very plausible that for $t \rightarrow \infty$, $\phi_N(\vec{R}, t)$ will go over into the microcanonical distribution

$$\phi_0(\vec{R}) = \frac{1}{S_N(\sqrt{N})} \quad (2)$$

($S_N(r)$ = surface area of N-dimensional sphere of radius r), which leads for the one-particle distribution to :

$$f_j^{(N)}(x) \sim \left(1 - \frac{x^2}{N}\right)^{\frac{N-3}{2}} \quad \text{as } t \rightarrow \infty$$

which in turn gives the M.B. distribution for $N \rightarrow \infty$

$$f_1(x) = \frac{1}{\sqrt{2\pi}} e^{-x^2/2} \quad (3)$$

The approach to (2) will be monotonic as can be seen by an analogue of the H-theorem. In fact one does not need the function

$$H(t) = \int \phi \log \phi \, dS \quad (4)$$

one can show the monotonic decrease already for the simpler quantity

$$K(t) \equiv \int \phi^2 \, dS \quad (5)$$

where $dS = dx_1 \dots dx_2 =$ element of surface area (on the sphere).

In fact

$$\frac{dK}{dt} = \frac{v}{N} \int_{-\pi}^{+\pi} d\theta F(\theta) \sum_{ij} \int \dots \int dS \phi(R,t) \{ \phi(A_{ij}(\theta)R,t) - \phi(R,t) \}$$

Put:

$$A_{ij}(\theta)R = R' \quad , \quad R = A_{ij}(-\theta)R'$$

Use R' and $\theta' = -\theta$ as new variables, and add the new result to the original form and divide by two; one gets then :

$$\frac{dK}{dt} = -\frac{v}{2N} \int_{-\pi}^{+\pi} d\theta F(\theta) \sum_{ij} \int \dots \int dS \{ \phi(A_{ij}R,t) - \phi(R,t) \}^2$$

$$\Rightarrow \frac{dK}{dt} \leq 0,$$

and the equality sign is only obtained for the uniform distribution.

The proof for $H(t)$ goes exactly the same way; in fact any function of ϕ which is concave upward would do. The exceptional property of the H-function is that with the Boltzmann property, clearly

$$\int \dots \int dS \phi \log \phi \rightarrow \text{const.} + N \int_{-\infty}^{+\infty} dx f \log f \quad (7)$$

which is what one expects for the entropy of an ideal gas, and which shows the connection between the Gibbs and the Boltzmann H-functions.

It still needs further argument to show rigorously that "any" $\phi(\vec{R}, t)$ goes over into the uniform distribution as $t \rightarrow \infty$. Kac was able to do this in the following sense: he proved that for every integrable function $\chi(\vec{R})$ on the sphere

$$\lim_{t \rightarrow \infty} \int \phi(\vec{R}, t) \chi(\vec{R}) dS = \frac{\int \chi(\vec{R}) dS}{S_N(N)}$$

15. - The relaxation time.

It would be of interest to know the spectral decomposition of the operator J^2 in the master equation,

$$\frac{\partial \phi}{\partial t} = -J^2 \phi,$$

which can be written as:

$$J^2 = \frac{K}{2N} \int_{-\pi}^{+\pi} d\theta F(\theta) \sum_{ij} (e^{i\theta L_{ij}} - 1), \quad (8)$$

where $L_{ij} = \frac{1}{\sqrt{1-x_i^2}} (x_i \frac{\partial}{\partial x_j} - x_j \frac{\partial}{\partial x_i})$ is the infinitesimal rotation operator. The question of the spectrum of J^2 has not been quite settled yet. Clearly zero is an eigenvalue, with eigenfunction $\phi = \text{const.}$, and the other eigenfunctions must be parical harmonics on the N-dimensional sphere. Let $H_K(x_1, \dots, x_N)$ be the solid harmonics of degree K,

which are in addition symmetric in x_1, x_2, \dots, x_N . There may be several of them which are linearly independent, which is indicated by the index k . Clearly ψ_k will be a linear combination of such spherical harmonics of the same degree, so that for each k one has to solve a finite secular problem to find the spectrum. This seems feasible, but has not been accomplished yet. One can argue that if functions $\psi_k(R)$ which fulfill the Boltzmann property are a sufficiently complete set of functions, then the spectrum of Ω should be the same as the spectrum of the Boltzmann non-linear collision operator. This spectrum in turn should be, for the first eigenvalues (which determine the last stages of the approach to equilibrium when the deviation from equilibrium has already become small), identical with the spectrum of the linearized Boltzmann equation, obtained by putting

$$f(x, t) = \frac{1}{\sqrt{\pi}} e^{-x^2/2} \{1 + h(x, t)\}$$

and neglecting quadratic terms in h . This gives :

$$\frac{\partial h}{\partial t} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dy e^{-y^2/2} \int_{-\infty}^{\infty} d\theta F(\theta) \{h(x + \theta) + h(y + \theta, t) + h(-x + \theta) + h(-y + \theta, t) - h(x) - h(y)\} = B_k(h)$$

(9)

This is the linearized form of the Boltzmann equation

$$\frac{\partial f}{\partial t} = B(h) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} d\theta F(\theta) \{h(x + \theta) + h(y + \theta, t) - f(x) - f(y)\}.$$

It is easy to prove that the eigen-values of $B_k(h)$ are the Hermite polynomials

$$h_k(x) = H_k\left(\frac{x}{\sqrt{2}}\right) = \frac{1}{\sqrt{2}} \left(\frac{x}{\sqrt{2}}\right)^k + \dots + \frac{(-1)^m}{k! (k-2m)!} \left(\frac{x}{\sqrt{2}}\right)^{k-2m}$$

(defined with e^{-x^2} as weight function for $H_k(x)$).

Using the addition theorem :

$$H_k(a \cos \theta + b \sin \theta) = \sum_{l=0}^k \binom{k}{l} \cos^l \theta \sin^{k-l} \theta H_k(a) H_{k-l}(b),$$

one easily finds for the spectrum :

$$\lambda_k = -v \int_{-\pi}^{+\pi} d\theta F(\theta) \left\{ 1 - \delta_{k0} + \cos^k \theta + (-1)^k \sin^k \theta \right\}. \quad (10)$$

The eigenvalue zero is doubly degenerate ($k = 0, k = 2$) corresponding to the conservation of number and energy. All other eigenvalues are negative, and have the value $v \int_{-\pi}^{+\pi} F(\theta)$ as limit point. For instance with $F(\theta) = 1$ for $-\pi/2 < \theta < \pi/2$ zero otherwise, one gets :

$$\lambda_0 = \lambda_2 = 0, \quad \lambda_{2n} = -\pi v \left[1 - \frac{1}{\pi} \frac{\Gamma(n + \frac{1}{2})}{\Gamma(n+1)} \right]$$

$$\lambda_{2n+1} = -\pi v \left[1 - \frac{1}{\pi} \frac{\Gamma(n+1)}{\Gamma(n + \frac{1}{2})} \right].$$

The even and odd λ 's form monotonic decreasing sequences with $-\pi v$ as limit point. The eigenvalue nearest to zero is $\lambda_1 = -\pi v/2$ which is therefore the analogue of the inverse of the relaxation time.

Larger disturbances from equilibrium will die down with exponential factors which will consist of linear combinations of the eigenvalues λ_n . This may well produce an almost continuous spectrum beyond a value which must be bigger than $2\lambda_1$. A few discrete values, and especially λ_1 itself, will clearly remain.

16. - Final Remarks.

The master equation approach shows conclusively, in my opinion, that the kinetic method of Boltzmann, properly interpreted, is in harmony with the statistical method and with the ideas of Gibbs. It leads to interesting mathematical problems, which still need a lot of work. However, there remains the basic question :

What is the relation between the master equation $\dot{\phi} = \Omega \phi$ and the

basic dynamical equation $\partial_t \rho = \{H, \rho\}$ (Liouville theorem), which determines the streaming over the energy surface ?

In other words : how can one "derive" the probability assumptions from the special features which characterizes the streaming under the influence of the short range intermolecular forces? Clearly what the master equation implies, is that with sufficient dilution, one can omit the intermolecular forces in H , and replace the streaming by the "jumping" with a probability determined by the Stozzahl Ansatz, i.e. the "master equation" approach is, strictly, applicable only to an ideal gas.

Because the connection with the dynamics is not established, the master equation approach does not allow one to answer the questions of physical interest :

- 1) What are the limitations of the kinetic method, especially with regard to rapidly varying phenomena (high frequency sound, for instance)?
- 2) How should one extend the kinetic method so as to take triple and higher multiple collisions into account, (i.e. to dense systems)?

The Hydrodynamical Equations

17. - The general conservation laws.

Going back to the Boltzmann equation with outside forces :

$$\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x_x} + v_y \frac{\partial f}{\partial y} = \int d\vec{\xi} \int d\Omega g^2 (g \cdot \theta) (f' f'_1 - f f_1) \quad (1)$$

I would like to outline the further development (due to Maxwell-Chapman, Lorentz-Hilbert-Enskog) partially because it still is the only rigorous theory for a class of non-equilibrium phenomena, and also in order to point out the peculiar features of the approximation method.

The first step is to derive from (1) the so-called transport equation for a quantity $\phi(x, y, z, t)$ which a molecule can carry "on its back". Defining :

$$\bar{\phi}(x, y, z, t) \equiv \frac{\int \phi f d\vec{v}}{\int f d\vec{v}} = \frac{1}{n} \int \phi f d\vec{v},$$

where $n(x, y, z; t)$ = number density ($n m = \rho$), one gets :

$$\begin{aligned} \frac{\partial}{\partial t} (n \bar{\phi}) + \frac{\partial}{\partial x_x} (n \bar{v}_x \bar{\phi}) - n v_x \frac{\partial \bar{\phi}}{\partial x_x} \\ = \frac{1}{n} \int d\vec{v} \int d\vec{\xi} \int d\Omega g^2 (g \cdot \theta) (\phi \cdot \phi' - \phi \phi_1) (f' f'_1 - f f_1). \end{aligned} \quad (2)$$

For ϕ equal to any of the five quantities $m, mv_x, \frac{mv^2}{2}, (v_x^2 + v_y^2 + v_z^2)$ which are conserved in a collision, the right-hand side of (2) vanishes, and one gets the five general hydrodynamical equations :

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \text{div} (\rho \vec{u}) &= 0 \\ \rho \frac{D u_x}{D t} &= \rho \left(\frac{\partial u_x}{\partial t} + \vec{u} \cdot \text{grad} u_x \right) - \rho X_x - \frac{\partial P_{xx}}{\partial x_x} \end{aligned}$$

$$\rho \frac{D}{Dt} \left(\frac{Q}{\rho} \right) + \text{div } \vec{q} = -P_{\alpha\beta} D_{\alpha\beta} \quad (3)$$

where

$x_i = x, y, z$: coordinates

$S_i = (S, \eta, \zeta)$: velocity components

$u_i = u, v, w$: average velocity

$w_i = \bar{S}_i$

$U_i = U, V, W$ = thermal velocity

$= S_i - u_i$

$X_i = X, Y, Z$ = outside force (per unit mass)

$Q = \frac{1}{2} \rho \overline{U^2}$ = thermal energy density

$P_{ij} = \rho \overline{U_i U_j}$ = stress tensor

$q_i = \frac{1}{2} \rho \overline{U_i U^2}$ = heat current density

$D_{ij} = \frac{1}{2} \left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} \right)$ = rate of strain (deformation) tensor

and, as indicated,

$$\frac{D}{Dt} \equiv \frac{d}{dt} + u_\alpha \frac{\partial}{\partial x_\alpha}$$

The equations (3) express the conservation laws of number, impulse and energy, and are still an empty frame since we do not know yet how to express P_{ij} , q_i in terms of the average (flow) velocity, the density, and the temperature. In other words, one still has to derive the Newton and Fourier phenomenological laws for friction and heat conduction.

18. - The Hilbert-Enskog development (1).

To do this one has to solve the Boltzmann equation. Hilbert introduces a formal parameter θ , and writes :

$$f = \frac{1}{\theta} f^{(0)} + f^{(1)} + \theta f^{(2)} + \dots$$

In addition (this is Enskog's contribution) it is necessary to decompose

(1) Chapman and Cowling, "The Mathematical Theory of Non-uniform Gases".

the time

the time derivative in parts of successive order of approximation by writing :

$$\frac{\partial}{\partial t} = \frac{\partial_0}{\partial t} + \theta \frac{\partial_1}{\partial t} + \dots$$

Calling $D \equiv \frac{\partial}{\partial x} + X \frac{\partial}{\partial X}$, and the collision operator $J(f, f_1)$, one gets from (1), by equating equal powers of θ ,

$$J(f^{(0)}, f_1^{(0)}) = 0 \quad (4)$$

$$\left(\frac{\partial_0}{\partial t} + D\right) f^{(0)} = J(f^{(0)}, f_1^{(0)} + f^{(1)}, f_1^{(0)}) \quad (5)$$

$$\frac{\partial_1 f^{(0)}}{\partial t} + \left(\frac{\partial_0}{\partial t} + D\right) f^{(1)} = J(f^{(0)}, f_1^{(2)} + f^{(1)}, f_1^{(1)} + f^{(2)}, f_1^{(0)}) \quad (6)$$

etc.

a) First approximation.

The development is clearly so arranged that (4) is the first approximation, of which the general solution is :

$$f^{(0)} = n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2} \frac{m}{kT} [(v-u)^2 + (y-v)^2 + (z-v)^2]} \quad (7)$$

the local Maxwell distribution, which contains still the five macroscopic quantities n, u_i, T which are functions of $x, y, z; t$ and remain undetermined.

b) Second approximation.

Writing $f^{(1)} = f^{(0)} \phi^{(1)}$ one easily sees that (5) becomes :

$$\left(\frac{\partial_0}{\partial t} + D\right) \phi^{(1)} = -I(\phi^{(1)}) \quad (5a)$$

where $I(\phi)$ is the linear isotropic operator

$$I(\phi) = \left\{ d \frac{\partial}{\partial x} + d a_j I(g, \phi) (\phi + \phi' - \phi'' - \phi''') f^{(0)} f_1^{(0)} \right\}$$

Equation (5a) is an inhomogeneous integral equation for $\phi^{(1)}$. The homogeneous part has clearly as solutions the five conserved quantities $\Psi_1 = 1, \Psi_2 = \frac{v}{v}, \Psi_3 = \frac{y}{v}, \Psi_4 = \frac{z}{v}, \Psi_5 = \frac{v^2 + y^2 + z^2}{v^2}$.

In order that the inhomogeneous equation have a solution, the inhomogeneous part must be orthogonal to the five solutions Ψ_k . This leads to the five integrability conditions :

$$\left. \begin{aligned}
 \frac{\partial \rho}{\partial t} &= - \operatorname{div}(\rho \vec{u}) \\
 \frac{\partial \rho}{\partial t} &= - (\rho \operatorname{div} \vec{u}) + \rho \operatorname{div} \vec{u} - \frac{1}{\rho} \operatorname{grad} p \\
 \frac{\partial T}{\partial t} &= - u \operatorname{grad} T - \frac{1}{3} T \operatorname{div} \vec{u}
 \end{aligned} \right\} (5 b)$$

which are the ideal fluid, or first order hydrodynamical, equations for ρ , u_i , T , or as Enskog expresses it : in first order the time derivatives

$\frac{\partial \rho}{\partial t}$, $\frac{\partial u_i}{\partial t}$, $\frac{\partial T}{\partial t}$ must be taken to be given by the ideal hydrodynamical equations. One can also say that in first order one can calculate the average values in the general hydrodynamical equations (3) with the local Maxwell-Boltzmann distribution (7), giving the Euler equations

$$p_{ij}^{(0)} = p \delta_{ij}, \quad q_i^{(0)} = 0.$$

Note that $p = nkT$ is given by the ideal gas law. If (5b) is fulfilled (5a) has a solution, which is determined except for an arbitrary linear combination of the five solutions ψ_a of the homogeneous equation. However, we will omit this combination and make $f^{(1)}$ definite by requiring :

$$\int \psi_a f^{(1)} d\mathbf{v} = 0 \quad (5 c)$$

c) Solution of (5 a).

The left-hand side becomes, using (7) and eliminating the $\partial/\partial t$ terms with (5 b) ,

$$\begin{aligned}
 & \left(\frac{\partial}{\partial t} + D \right) f^{(1)} = \\
 & = f^{(0)} \left[\frac{\partial T}{\partial x_\alpha} \frac{1}{kT} \left(\frac{u_\alpha}{kT} U^2 - \frac{2}{3} \right) + \frac{u_\alpha}{kT} D_\alpha \left(U^2 U_\beta - \frac{1}{3} \delta_{\alpha\beta} U^2 \right) \right]
 \end{aligned}$$

From the linearity of the operator I it follows that one can decompose $\phi^{(1)}$ writing $f^{(0)} = Ae = \frac{1}{2kT} U^2$ one can put

$$\phi^{(1)} = - \frac{1}{AT} \frac{\partial T}{\partial x_\alpha} \Pi_\alpha - \frac{1}{A} \frac{D_\alpha}{kT} \Phi_{\alpha\beta} \Phi_{\alpha\beta}$$

where $\bar{\Pi}_i$, $\bar{\Phi}_{ij}$ are functions of the U_i determined by :

$$\left. \begin{aligned} I'(\bar{\Pi}_i) &= U_i \left(\frac{m}{2kT} U^2 - \frac{5}{2} \right) e^{-\frac{m}{2kT} U^2} \\ I'(\bar{\Phi}_{ij}) &= \left(U_i U_j - \frac{1}{3} \delta_{ij} U^2 \right) e^{-\frac{m}{2kT} U^2} \end{aligned} \right\} \quad (5 d)$$

and :

$$I'(\Psi) = \int d\vec{U}_1 \int d\Omega_g(g, \theta) (\Psi + \Psi' - \Psi'' - \Psi''') e^{-\frac{m}{2kT} (U^2 + U_1^2)}$$

is recognized as the linearized Boltzmann operator. Since I' is an isotropic operator, $\bar{\Pi}_i$ and $\bar{\Phi}_{ij}$ must be, respectively, an isotropic vector and an isotropic tensor in the velocity space U_i , so that they must have the form :

$$\bar{\Pi}_i = U_i \chi_a(U^2), \quad \bar{\Phi}_{ij} = \left(U_i U_j - \frac{1}{3} \delta_{ij} U^2 \right) \chi_b(U^2) \quad (5 e)$$

The two functions χ_a and χ_b are determined by (5 d). The solution is immediate if one knows the eigenfunctions and eigenvalues of the operator I . This is the case for Maxwell molecules; for other interactions one develops χ_a and χ_b in Sonine polynomials, which are the orthogonal eigenfunctions χ_a of $I(\chi_a)$ for Maxwell molecules. (See Equation (9), page 5). The resulting infinite set of linear equations can be solved by convergent series expansions, of which the parameter is a measure of the deviation of the force law from the $1/r^5$ repulsion.

d) Third approximation.

Putting $f^{(2)} = f^{(0)} \phi^{(2)}$, and keeping in mind that $(f^{(0)} f_{i'}^{(0)} \psi') = f_{i'}^{(0)} f_{i'}^{(0)} \psi'$, equation (6) becomes :

$$\frac{\partial_t f^{(2)}}{\partial t} + \left(\frac{\partial_0}{\partial t} + D \right) f^{(1)} - J(f^{(1)} f_{i'}^{(1)}) = -I[\phi^{(2)}] \quad (6 a)$$

Again the left-hand side is known and must be orthogonal to the five solutions:

Ψ_k of the homogeneous equation. Since clearly :

(by the "Boltzmann" transformation) and

$$\int \Psi_k \frac{\partial f^{(0)}}{\partial t} d\vec{\xi} = 0$$

because of (5a), one only has to fulfill :

$$\int \Psi_k \left(\frac{\partial f^{(0)}}{\partial t} + D f^{(0)} \right) d\vec{\xi} = 0 \quad (6b)$$

One can say that (6b) determines (note that $f^{(1)}$ is completely known) the first order time derivatives of n , u_i and T . One finds that the zero and first time derivatives together fulfill the Stokes-Navier or second order hydrodynamic equations, which therefore appear as the integrability conditions for the third approximation. The same equations are obtained by calculating the average values in the general hydrodynamical equations (3) using for the distribution function $f^{(0)} + f^{(1)}$. One finds:

$$P_{ij}^{(1)} = P \delta_{ij} - 2\mu (D_{ij} - 1/3 D_{kk} \delta_{ij}), \quad q_i^{(1)} = \nu \frac{\partial T}{\partial x_i}$$

which are the Newton and Fourier laws. When the stress tensor given by Newton's law is inserted in the equations of motion (the middle ones of (3)), the Navier-Stokes equations result. The viscosity coefficient μ and heat conduction coefficient ν are certain integrals over the functions

$\chi_a(U^2)$, $\chi_b(U^2)$ and in first approximation (exact for Maxwell molecules!) are given by :

$$\mu = \frac{5}{2} \frac{P}{4\pi n k T} \frac{1}{\int_0^\infty d g g^7 e^{-g^2} Q_{tr}(g)} \quad (8)$$

$$\nu = 5/2 \frac{c_v \mu}{\nu}$$

where g is the relative velocity in units $\sqrt{4 kT/m}$ and Q_{tr} is the so-called transport cross section :

$$Q_{tr}(g) = 2 \pi \int_0^\pi d\theta \sin^3 \theta I(g, \theta).$$

If the first order time derivatives of n , u_i and T are fixed by (6b), then

(6a) has a solution determined up to a linear combination of the ψ_i , which again we omit, fixing the $f^{(2)}$ by the requirements :

$$\int \psi_i f^{(2)} d\vec{s} = 0$$

The $f^{(2)}$ can then be determined by the same method as used for $f^{(1)}$, and in this way one can go on. The integrability conditions for the fourth approximation are the Burnett, or third order hydrodynamical equations, also obtainable from (3) by using $f^{(0)} + f^{(1)} + f^{(2)}$ in the calculation of the average values. They are still of the first order in the time derivatives but now contain higher order space derivatives of the macroscopic quantities ρ , u_i and T , and new gas constants analogous to μ and ν appear.

19. General discussion of the development

a. - The development can be said to be in powers of λ^2 where λ is of the order of the mean free path and the gradient operator acts on the macroscopic quantities. In fact, from (5d) one sees that $\phi^{(1)}$ contains terms of order :

$$\frac{1}{n} \frac{1}{T} \frac{\partial T}{\partial x} \approx \frac{\lambda}{T} \frac{\partial T}{\partial x}$$

and

$$\frac{1}{n} \frac{1}{2kT} \frac{\partial u}{\partial x} \approx \frac{\lambda}{\text{sound vel.}} \frac{\partial u}{\partial x}$$

where λ is some kind of collision cross section. The development is therefore in the uniformity of the macroscopic quantities ρ , u_i , T and one can say that the Hilbert parameter λ is a measure of the uniformity.

b. - The development is so arranged that at any stage the equations are of first order in the time derivatives of ρ , u_i and T (by leaving off the homogeneous solutions). Therefore the initial values of ρ , u_i and T determine the "state" of the gas. This macroscopic causality theorem (Hilbert) is of course not a theorem but an "Ansatz". It seems paradoxical because from the Boltzmann equation it clearly follows that one needs initially $f(\vec{s}, \vec{v}, \vec{r}, 0)$ (which contains of course much more information than the five moments $n(xyz)$, $u_i(xyz)$, $T(xyz)$ do.) to determine the further state of the gas.

One must expect, therefore, that an arbitrary initial velocity distribution $f(\vec{s}, \vec{v}, \vec{r}, 0)$ in a very short time (of order of the time between collisions, $\lambda \sqrt{\frac{kT}{m}}$) degenerates into a normal

state" determined through the local Maxwell-Boltzmann distribution by the macroscopic quantities. ρ , u_i , T , and that the further slow equalization or adjustment of the spatial non-uniformities proceeds according to the hydrodynamical equations and in harmony with the macroscopic causality requirement.

c. - The development does not distinguish between the magnitude of the disturbance and the scale of the disturbance from equilibrium. In any physical problem these can be well distinguished. For instance, in the propagation of sound they are measured by the intensity and the wavelength of the sound wave, respectively. Especially for the discussion of what happens at low pressures (that is, for large mean free paths) the Hilbert-Enskog development is not appropriate. For the theory of the transition between the "Clausius gas regime" (at moderate pressures) and the "Knudsen gas regime" (at very low pressures) it is better to make a straightforward perturbation expansion of the Boltzmann equation by putting :

$$f = f_0 (1 + h)$$

where f_0 is the complete equilibrium distribution and the perturbation h satisfies the linear homogeneous equation :

$$\frac{\partial h}{\partial t} + \sum_x \frac{\partial h}{\partial x_x} = J(h)$$

in the absence of outside forces. For various special cases this can be solved in detail, allowing for a discussion of the dependence on the scale or Knudsen number ($\approx \lambda / L$, where L = representative length) for small disturbances or small Mach number.

20. The idea of the virial expansion.

The classical result that the viscosity and heat conduction coefficients are independent of the pressure of the gas is clearly a consequence of the limitation to binary collisions. Presumably for higher densities one may expect that for slowly varying phenomena the Stokes-Navier equations remain valid, but that the μ (and ν) will become functions of the density, which are developable in the form :

$$\mu = \mu_0 + \mu_1 \rho + \mu_2 \rho^2 + \dots \quad (1)$$

analogous to the well-known virial development :

$$p = \rho kT \left(1 + \frac{B}{v} + \frac{C}{v^2} + \dots \right) \quad (2)$$

of the equation of state, with $v = \frac{V}{N} = \frac{m}{\rho}$. In (2) one knows how to express the virial coefficients in terms of the intermolecular force $\phi(r)$. One has :

$$B = -\frac{1}{2} \int d\vec{r} f(r) = 2\pi \int_0^\infty dr r^2 \left(1 - e^{-\frac{\phi(r)}{kT}}\right)$$

$$C = -\frac{1}{3} \int d\vec{r}_1 d\vec{r}_2 f(r_1) f(r_2) + (1^2 - 1)$$

(3)

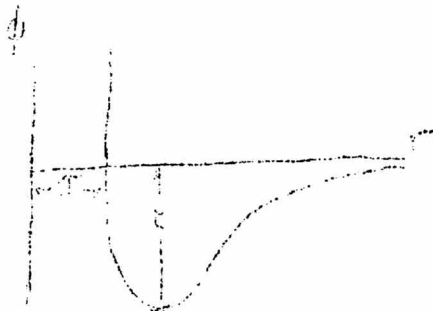
And so on! B involves the interaction of a pair of molecules, C of a triple, and so forth.

The μ_0 is the viscosity coefficient derived in the previous section :

$$\mu_0 = \frac{5}{8} \sqrt{\pi m kT} \frac{1}{\int_0^\infty dg g^3 e^{-g^2} Q_{tr}(g)}$$

(g = relative velocity in units $\sqrt{4kT/m}$; $Q_{tr} = 2\pi \int_0^\pi d\theta \sin^2 \theta I(g\theta)$)

It involves through the $I(g, \theta)$ the intermolecular force $\phi(r)$ between a pair of molecules. It is therefore related to the second virial coefficient B. The relation is very implicit, but by assuming a form for $\phi(r)$, as for instance a two-parameter Lennards-Jones potential



$$\phi(r) = 4\epsilon \left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6 \right]$$

one can calculate $B(T)$ and $\mu_0(T)$ and see whether one can reproduce the data adapting ϵ and r_0 . Such calculations have been made by Hirschfelder and coworkers with success. The agreement is very good, especially for the inert gases.

Analogously one must expect that μ_1 involves the interaction of the molecules in triples, so that it would be related to the third virial coefficient C. However, no general formulae for μ_1, μ_2, \dots are known.

21. The virial expansion for the equilibrium state.

Although this is well known, and a little aside from our main

topic, I will give a derivation of (2) and (3) by following Bogolubov (Journal of Phys. 10, 256, 1946). It is an introduction to the method he proposes in a following paper (Journal of Phys. 10, 265, 1946) for the virial expansion of non-equilibrium properties. Start from the canonical distribution in co-ordinate space

$$D_N(\vec{q}_1, \dots, \vec{q}_N) = \frac{1}{Q_N} e^{-U_N/KT}, \quad (4)$$

$$U_N \equiv \sum_{i < j} \phi(|\vec{q}_i - \vec{q}_j|); \quad Q_N = \int \dots \int d\vec{q}_1 \dots d\vec{q}_N e^{-U_N/KT}$$

D_N is symmetric in $q_1 \dots q_N$, and normalized to unity. One can form partial distribution functions by integrating: let $\frac{1}{V^s} F_s(q_1 \dots q_s)$ be the probability of finding an s-tuple in $q_1 \dots q_s$:

$$F_s = V^s \int \dots \int D_N d\vec{q}_{N+1} \dots d\vec{q}_N.$$

Now observe that D_N fulfills

$$\frac{\partial D_N}{\partial q_{i\alpha}} + \frac{1}{KT} \frac{\partial U_N}{\partial q_{i\alpha}} D_N = 0 \quad (\alpha = x, y, z) \quad (5)$$

by logarithmic differentiation of (4). Integrate (5) over $q_{s+1} \dots q_N$; then one gets for F_s in the limit $N \rightarrow \infty$, $V \rightarrow \infty$, $v = V/N$ finite:

$$\frac{\partial F_s}{\partial q_{i\alpha}} + \frac{1}{KT} \frac{\partial U_s}{\partial q_{i\alpha}} F_s + \frac{1}{KT} \int d\vec{q}_{s+1} \dots \frac{\partial \phi(|\vec{q}_i - \vec{q}_{s+1}|)}{\partial q_{i\alpha}} F_{s+1} = 0 \quad (6)$$

where :

$$U_s = \sum_{i < j=1}^s \phi(|q_i - q_j|) \equiv \sum \phi_{ij}$$

Proof :

$$U_N = U_s + \sum_{s < i < j \leq N} \phi_{ij} + \sum_{i < s < j, \dots} \phi_{ij}$$

From the U_s part of U_N in (5) one gets the first two terms in (6). If i, j are both $> s$, differentiation by $q_{i\alpha}$ gives zero; the only terms

remaining which give a non-vanishing contribution are ϕ_{ij} , with $j > s$.

Because of the symmetry of D_N , one gets for all the $N - s$ values of j the same expression, namely :

$$\frac{1}{kTV} \int dq_{s+1} \frac{\partial \phi_{i,s+1}}{\partial q_{ix}} F_{s+1}$$

so that in the limit we have (6) $\left(\frac{N-s}{V} \rightarrow \frac{1}{v} \right)$.

One can now say that the hierarchy of eqs. (6) for the successive distribution functions must be solved with the conditions :

$$F_s(q_1 \dots q_s) - \prod_{i=1}^s F_i(q_i) \rightarrow 0 \quad (7)$$

if all $|\bar{q}_i - v_j| \rightarrow \infty$

Now make the development in powers of $\frac{1}{v}$:

$$F_s = F_s^{(0)} + \frac{1}{v} F_s^{(1)} + \frac{1}{v^2} F_s^{(2)} + \dots \quad (8)$$

Then one gets from (6) :

$$\left. \begin{aligned} \frac{\partial F_s^{(0)}}{\partial q_{ix}} + \frac{1}{kT} \frac{\partial \phi_s}{\partial q_{ix}} F_s^{(0)} &= 0 \\ \frac{\partial F_s^{(r)}}{\partial q_{ix}} + \frac{1}{kT} \frac{\partial \phi_s}{\partial q_{ix}} F_s^{(r)} + \frac{1}{kT} \int dq_{s+1} \frac{\partial \phi_{i,s+1}}{\partial q_{ix}} F_{s+1}^{(r-1)} &= 0 \end{aligned} \right\} (9)$$

which can now be solved successively. The development (8) must also be used in (7), giving :

$$\begin{aligned} F_s^{(0)}(q_1 \dots q_s) - \prod_{i=1}^s F_i^{(0)}(q_i) &\rightarrow 0, \\ F_s^{(1)} &\rightarrow \sum_{i=1}^s F_i^{(1)}(q_i) \prod_{k \neq i} F_k^{(0)}(q_k), \end{aligned} \quad (10)$$

etc. Finally, one must require, since $\int_1^s F_1(q) dq = V$, that :

$$\lim_{V \rightarrow \infty} \frac{1}{V} \int_1^s F_1^{(0)}(q) dq = 1 \quad \lim_{V \rightarrow \infty} \frac{1}{V} \int_1^s F_1^{(1)}(q) dq = 0 \quad (11)$$

Eqs. (9), (10), (11), suffice to determine all $F_s^{(r)}$.

For instance in zerorth approximation : from (9) it follows, putting:

$$F_s^{(0)} = C_s^{(0)} (q_1 \dots q_s) \exp(-U_s/kT)$$

that

$$\frac{\partial C_s^{(0)}}{\partial q_{s+1}} = 0$$

so $C_s^{(0)} = \text{const.}$ (because of symmetry requirement). From boundary condition (10),

$$C_s^{(0)} = (C_1^{(0)})^s, \text{ and from normalization (11) } C^{(0)}, \text{ so :}$$

$$F_s^{(0)} = 1, \quad F_s^{(0)} = \exp(-U_s/kT). \quad (12)$$

In first approximation, putting again $F_s^{(1)} = C_s^{(1)} \exp(-U_s/kT)$, one gets from (9), using the symmetry requirement :

$$C_s^{(1)} = \left\{ dq_{s+1} \left\{ e^{-\frac{1}{kT} \sum_{i=1}^s \phi_{i,s+1}} - 1 \right\} + B_s \right.$$

B_s is a constant. If $|q_i - q_s| \rightarrow \infty$, for $i = 1, 2, \dots, s$, one sees that :

$$F_s^{(1)} \rightarrow \sum_{i=1}^s \int dq_{s+1} \left(e^{-\frac{1}{kT} \phi_{i,s+1}} - 1 \right) + B_s$$

Since :

$$F_1^{(1)} = C_1^{(1)} = \int dq_2 \left\{ e^{-\frac{1}{kT} \phi_{1,2}} - 1 \right\} + B_1,$$

one gets from the boundary condition (10), that $B_s = sB_1$. Finally from the normalization condition (11) :

$$B_1 = - \int dq_2 \left\{ e^{-\frac{1}{kT} \phi_{1,2}} - 1 \right\}$$

giving :

$$F_1^{(1)} = 0, \quad F_2^{(1)} = e^{-\frac{U_2}{kT}} \left\{ d q_{s+1} \left\{ \prod_{i=1}^s (1 + f(q_i - q_{s+1})) \right. \right. \\ \left. \left. - 1 - \sum_{i=1}^s f(q_i - q_{s+1}) \right\} \right\} \quad (13)$$

where for abbreviation :

$$f(r) = e^{-\phi(r)/kT} - 1$$

And so on. To get the equation of state one only has to use the general virial theorem which leads to :

$$\frac{PV}{kT} = 1 - \frac{1}{6kT} \cdot \frac{1}{V} \int d^3r r \cdot \phi(r) F_2(r)$$

where $r = q_1 - q_2$, in which one must then substitute the successive approximation for $F_2(q_1, q_2)$ which one has found. Using the zeroth and 1st approximations (12) and (13) gives the equation of state up to the third virial coefficient.

22. The Kirkwood - Born - Green development.

For non-equilibrium situations the probability distribution $D_N(x_1, \dots, x_N, t)$ in Γ -space ($x_i \equiv \vec{q}_i, \vec{p}_i$) is of course not known.

All we do know is that D_N must be symmetric in x_1, x_2, \dots, x_n and that it fulfills Liouville's equation :

$$\frac{\partial D_N}{\partial t} = \{H, D\} \quad (14)$$

$$\left(\{H, D\} = \sum_{i=1}^N \left(\frac{\partial H}{\partial q_i} \frac{\partial D}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial D}{\partial q_i} \right), \quad H = \sum_{i=1}^N [T(p_i) + U(q_i)] + \sum_{\langle i,j \rangle} \phi(r_{ij}) \right),$$

$T(p) = \frac{p^2}{2m}$; $U(q) =$ outside force, in which one must include the "wall potential" is the gas is enclosed in a vessel of volume V .

One still can introduce the partial distributions :

$$\frac{1}{V^s} F_s(t, x_1, \dots, x_s) = \int \dots \int D_N dx_{s+1} \dots dx_N$$

and then (14) is equivalent to a hierarchy of equations. These were written out at about the same time by Kirkwood, Born and Green, and Bogolubov, and I will follow the last. In the limit $N \rightarrow \infty$, $V \rightarrow \infty$, $v = V/N$ finite, one gets :

$$\frac{\partial F_s}{\partial t} = \{H_s, F_s\} + \frac{1}{v} \int dx_{s+1} \left\{ \sum_{i=1}^s \phi_{i,s+1}, F_{s+1} \right\}. \quad (15)$$

H_s is the Hamiltonian of the s-tuple of particles :

$$H_s = \sum_{i=1}^s T(p_i) + \sum_{1 \leq i < j \leq s} \phi_{ij}$$

where there are no outside forces, and the wall potential can also be omitted if V is very large.

The proof of (15) is quite similar to that of (6). In fact one gets immediately :

$$\frac{\partial F_s}{\partial t} = \{H_s, F_s\} + V^s \int dx_{s+1} \dots dx_N \left\{ \sum_{i=1}^N \{T(p_i) + U(q_i) + \sum_{\substack{j=1 \\ j \neq i}}^N \phi_{ij}\}, D \right\}.$$

Since D must be assumed to vanish for large p_i and q_i , one easily sees that in the last term only the terms with the intermolecular potential with $i \leq s$ and $j > s$ will give a contribution. For such a term :

$$\begin{aligned} V^s \int \dots \int dx_{s+1} \dots dx_N \{ \phi(r_{ij}), D \} &= \\ &= V^s \int dx_j \frac{\partial \phi}{\partial q_i} \frac{\partial}{\partial p_i} \{ \dots \} D dx_{s+1} \dots dx_N \end{aligned}$$

where the prime means that dx_j is omitted. Because of the symmetry of D , one can always put $j = s+1$ and one has $N - s$ equal terms :

$$\begin{aligned} &V^s \int dx_{s+1} \frac{\partial \phi(q_i - q_{s+1})}{\partial q_i} \frac{\partial}{\partial p_i} \{ \dots \} D dx_{s+2} \dots dx_N \\ &= \frac{1}{v} \int dx_{s+1} \left\{ \phi(|q_i - q_{s+1}|), F_{s+1} \right\}. \end{aligned}$$

Altogether one gets therefore :

$$\frac{N-s}{V} \int dx_{s+1} \left\{ \sum_{i=1}^s \phi_{i,s+1}, F_s \right\}$$

which in the limit gives the last term in (15).

Of course no real advance has been made. The set of equations (15) is equivalent to the Liouville theorem. Note that for $s = 1$, (15) becomes :

$$\frac{\partial F_1(q, p, t)}{\partial t} = -\frac{p_x}{m} \frac{\partial F_1}{\partial q_x} + \int \frac{d\vec{p}_1}{V} \int d\vec{q}_1 \frac{\partial \phi(|\vec{q} - \vec{q}_1|)}{\partial q_x} \frac{\partial F_2(q, q_1, p, p_1)}{\partial p_x} \quad (15a)$$

which "smells" like the Boltzmann equation, but the connection is still far from clear.

The ideas of Bogolubov . II.

23. General ideas.

One is tempted to imitate the virial expansion for the equilibrium state, starting now from eq. (15). This is not a good idea, because in the zeroth approximation one would get :

$$\frac{\partial F^{(0)}}{\partial t} = \{ H_0, F^{(0)} \}$$

which means that $F^{(0)}$ changes in time according to the interactions between the s particles, without collisions with other particles. Such an expansion can therefore be valid only for very short times, small compared to the time $t_0 = \lambda / U_{av}$ between collisions. In fact the order of magnitude of successive terms in such an expansion after time t would be :

$$\frac{r_0^3}{V} \frac{t}{\lambda / U_{av}} \approx n r_0^3 U_{av} t \approx \frac{U_{av} t}{\lambda} = \frac{t}{t_0}$$

($n = 1/v =$ number of particles / cc ; $r_0 =$ range of inter-molecular forces ; $\lambda \approx \frac{1}{n \sigma}$ = mean free path).

Yet one must somehow obtain the Boltzmann equation in first approximation. One might think that at low densities somehow the state of the gas can be described by the first distribution function $F_1(x, t)$ and that all higher ones are products of F_1 ; at higher densities one would need both F_1 and F_2 , the higher distribution should be expressible in these, and F_2 , so on. I thought along these lines for some time, and also Kirkwood follows this idea. Success has been very meagre; at best one can "derive" the Boltzmann equation from (15a), but no one has really gone any further.

Bogolubov argues in a different way. He distinguishes in the temporal development of the gas three stages :

a. Initial mixing : from an arbitrary initial distribution $D(x_1 \dots x_n, 0)$ he supposes that very quickly (in a time of the order

$\tau_0 = r_0 / U_{av} =$ the interaction time, or time of a collision; τ_0 is very small compared to $t_0 = \lambda / U_{av}$ which is the mean free time or time between collisions, at least for moderate densities), a (first) "smoothing" process occurs, and that from then on the development depends only on $F_1(x, t)$. The initial detailed knowledge is lost, so that after this initial period the further development depends only on F_1 .

b. Kinetic stage. This describes the development of F_1 , for which one assumes a kinetic equation of the form :

$$\frac{\partial F_1}{\partial t} = A(x, F_1) = A_0(x, F_1) + \frac{1}{V} A_1(x, F_1) + \frac{1}{V^2} A_2(x, F_1) + \dots$$

(1)

while all the higher probability distributions depend on the time only through F_1 . One puts :

$$F_s(t, x_1, \dots, x_s) = F_s(x_1, \dots, x_s; F_1) = F_s^{(0)}(x_1, \dots, x_s; F_1) + \frac{1}{t} F_s^{(1)}(x_1, \dots, x_s; F_1) + \dots \quad (2)$$

for $s \geq 2$. One keeps the eqs. (15) relating the distribution functions, and the problem is to find $A(x, F_1)$. It must of course be so arranged that A_0 describes the streaming, A_1 the Boltzmann binary collision term, A_2 the triple collision term, etc.

After a while, in a time of order t_0 (the mean free time), but small compared to macroscopic relaxation times, a second smoothing process occurs, so that from then on one does not need F_1 , but only the five moments ρ , \vec{u} , and T . Again one can say that some knowledge is lost, and that the further development now depends only on the values of ρ , \vec{u} , and T after this second period.

c. Hydrodynamical stage. This describes the development of ρ , \vec{u} , and T , for which one assumes hydrodynamical eqs. of the general form :

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= R(\vec{q}, \rho, \vec{u}, T) \\ \frac{\partial \vec{u}}{\partial t} &= \vec{U}(\vec{q}, \rho, \vec{u}, T) \\ \frac{\partial T}{\partial t} &= \Phi(\vec{q}, \rho, \vec{u}, T). \end{aligned} \quad (3)$$

One keeps the kinetic equation (1) previously derives, but one assumes that F_1 depends on the time only through ρ , \vec{u} , T , so :

$$F_1(t, \vec{q}, \vec{p}) = F_1(\vec{q}, \vec{p}, \rho, \vec{u}, T).$$

The problem is to find the functions R , \vec{U} , Φ . Like Hilbert and Enskog, Bogolubov uses an uniformity parameter in all functions are developed, so that this part is rather analogous to the Hilbert-Enskog development, except that now in principle the virial type of development can be obtained for the viscosity and heat conduction coefficients also. There are no results as yet. But there is a whole program !

24. The kinetic equation.

Using the general equation (15) :

$$\frac{\partial F_s}{\partial t} = \{H_s, F_s\} + \frac{1}{t} \left\{ dx_{s+1} \left\{ \sum_{i=1}^s \phi(q_i - q_{s+1}) F_{s+1} \right\} \right\}$$

and the expansions (1) and (2), one gets for S = 1 :

$$\begin{aligned}
 A_0(x_1; F_1) &= \left\{ T(p), F_1 \right\} = - \frac{p_1 \Delta}{m} \frac{\partial F_1}{\partial q_1} \\
 A_1(x_1; F_1) &= \left\{ dx_2 \left\{ \phi_{12}, F_2^{(1)}(x_1, x_2; F_1) \right\} \right\}
 \end{aligned}
 \tag{4}$$

etc. A_s is therefore the streaming term, as expected. For s \geq 2, one gets :

$$\left\{ H_0, F_1^{(1)} \right\} - D_0 F_1^{(1)} = 0 \tag{5a}$$

$$\left\{ H_0, F_2^{(1)} \right\} - D_0 F_2^{(1)} - D_1 F_1^{(1)} + \left\{ dx_{s+1} \left\{ \sum_{i=1}^s \phi_{i, s+1}, F_{s+1}^{(1)} \right\} \right\} \tag{5b}$$

etc. Here the differentiation operation D_r acting on any function $\Psi(x_1, \dots, x_s; F_1)$ means

$$D_r \Psi \equiv \frac{\partial \Psi}{\partial F_1} A_r(x_1, F_1) \tag{6}$$

since all time dependences occur through F_1 . The program is now to solve equation (5a), which then from (4b) would give A_1 , then solve (5b) which would give A_2 , etc.

However, to solve (5a) one needs some boundary conditions. Bogolubov demands that for any function F_1 and for all F_s ($s \geq 2$) :

$$\lim_{T \rightarrow \infty} \left\{ F_1(x_1, \dots, x_s, \frac{1}{T} F_1) - \prod_{i=1}^s F_1(x_i) \right\} \rightarrow 0$$

for $T \rightarrow \infty$ (7)

Excursion on the operator $S_t^{(s)}$:

Suppose that the motion of the s particles under the influence of their mutual interactions (with Hamiltonian H_s) is solved, so that one knows the phases :

$$x_i = x_i(t, x_1, \dots, x_s) \quad (i = 1, 2, \dots, s)$$

of the s points as functions of t and the initial phases $x_1 \dots x_s$.

Define the "streaming operator" $S_t^{(s)}$ acting on a function $f(x_1 \dots x_s)$ by :

$$S_t^{(s)} f(x_1 \dots x_s) \equiv f(x_1, x_2, \dots, x_s). \quad (8)$$

In particular, of course, $S_t^{(1)} x_i = X_i$, and also clearly

$$S_{t_1+t_2}^{(s)} = S_{t_1}^{(s)} \cdot S_{t_2}^{(s)}. \quad \text{With the help of } S_t^{(s)} \text{ one can "integrate"}$$

partial differential equations of the form :

$$\frac{\partial \phi(t, x_1 \dots x_s)}{\partial t} = \{H_s, \phi\} + f(t, x_1 \dots x_s) \quad (9)$$

where f is known. Namely, one can write equation (9) in the form

$$\frac{D\phi}{Dt} = f(t, x_1 \dots x_s) \quad \left(\frac{D}{Dt} = \text{substantial differentiation quotient}\right).$$

Therefore, $\phi(t, x_1 \dots x_s) = \phi(0, x_{10} \dots x_{s0}) + \int_0^t (\tau, x_{1\tau} \dots x_{s\tau})$,

where the initial positions $x_{10} \dots x_{s0}$ and the positions at time τ , $x_{1\tau} \dots x_{s\tau}$, must be considered as functions of t and the $x_1 \dots x_s$ (which are the positions at time t). Therefore :

$$\begin{aligned} \phi(0, x_{10} \dots x_{s0}) &= \phi(0 S_{-t}^{(1)} x_1, S_{-t}^{(1)} x_s) \\ &= S_{-t}^{(s)} \phi(0, x_1, \dots, x_s) \end{aligned}$$

and analogously :

$$f(\tau, x_{1\tau} \dots x_{s\tau}) = S_{-(t-\tau)} f(\tau, x_1 \dots x_s).$$

Hence the solution of (9) can be written in the form :

$$\phi(t, x_1 \dots x_s) = S_{-t}^{(s)} \phi(0, x_1 \dots x_s) + \int_0^t d\tau S_{-(t-\tau)}^{(s)} f(\tau, x_1 \dots x_s). \quad (10)$$

Condition (7) somehow says that before the s -tuple collision the F is a product of the $F_1(x_i)$. I must say that it is not clear to me, but it works, and it is perhaps best to show how one can now determine the $A_i(x; F_1)$ successively.

First note that with the expansion (2), the condition (7) is equivalent to :

$$S_{-T}^{(s)} \left\{ F_s^{(s)}(x_1 \dots x_s; S_T^{(1)} F_1) - \prod_{i=1}^s S_T^{(1)} F_i(x_i) \right\} \rightarrow 0 \quad \text{as } T \rightarrow \infty,$$

$$S_{-T}^{(s)} F_s^{(1)}(x_1 \dots x_s; S_T^{(1)} F_1) \rightarrow 0 \quad \text{as } T \rightarrow \infty \quad (7a)$$

etc. Now one can start.

First approximation.

We have to solve (5a). Since (5a) must hold for any function F_1 , put in $F_s^{(0)}$ the function $S_{-T}^{(1)} F_1$ for F_1 . Then one sees that

$$D_0 F_s^{(0)}(x_1, \dots, x_s; S_{-T}^{(1)}) = \frac{\partial}{\partial T} F_s^{(0)}(x_1, \dots, x_s; S_{-T}^{(1)} F_1)$$

because

$$\frac{\partial}{\partial T} F_s^{(0)} = \frac{\partial F_s^{(0)}}{\partial (S_{-T}^{(1)} F_1)} \cdot \frac{\partial}{\partial T} S_{-T}^{(1)} F_1$$

and

$$\frac{\partial}{\partial T} S_{-T}^{(1)} F_1 = \{H_1, F_1\} = \{T(P_1) F_1\} = A_0(x; F_1)$$

so one just gets $D_0 F_s^{(0)}$ according to the definition (6) of the operator D_0 . Therefore (5a) becomes :

$$\frac{\partial}{\partial T} F_s^{(0)}(x_1, \dots, x_s; S_{-T}^{(1)} F_1) = \{H_{S_1}, F_s^{(0)}(x_1, \dots, x_s; S_{-T}^{(1)} F_1)\}$$

whence (using the first term of the general solution (10)),

$$F_s^{(0)}(x_1, \dots, x_s; S_{-T}^{(1)} F_1) = S_{-T}^{(1)} F_s^{(0)}(x_1, \dots, x_s; F_1).$$

so :

$$F_s^{(0)}(x_1, \dots, x_s; F_1) = S_{-T}^{(1)} F_s^{(0)}(x_1, \dots, x_s; S_{+T}^{(1)} F_1).$$

This holds for arbitrary T , and since the left-hand side is independent of T , one can go to $T \rightarrow \infty$, and using (7a) one gets :

$$S_{+T}^{(1)} F_1(x) = F_1\left(\frac{x}{m} + \frac{p}{m} T, p\right),$$

On the other hand :

$$S_T^{(1)} F_i(x_i) = F_i\left(\psi_i + \frac{P_i}{m}, P_i\right),$$

so :

$$S_{-T}^{(s)} \prod_i S_T^{(i)} F(x_i) = \prod_i F_i\left(S_{-T}^{(s)} \psi_i + \frac{\tau}{m} \sum_{-T}^{(s)} P_i, S_{-T}^{(s)} P_i\right).$$

Call now :

$$P_i^{(s)}(x_i, x_s) \equiv \lim_{T \rightarrow \infty} S_{-T}^{(s)} P_i \quad (11)$$

$P_i^{(s)}$ is the constant initial impulse of the i-th particle in the s-tuple collision (governed by H_s), which leads to the configuration x_1, \dots, x_s at time zero. The transition from p_i to P_i goes fast (in a time of order of the interaction time $T_c = r_0/U_{av}$), at least for small s), and since :

$$\sum_{-T}^{(s)} \psi_i = \psi_i - \frac{1}{m} \int_0^T d\tau' \sum_{-T}^{(s)} P_i$$

one can see that for $T \rightarrow \infty$, $\sum_{-T}^{(s)} \psi_i + \frac{\tau}{m} \sum_{-T}^{(s)} P_i$ will go to the limit :

$$Q_i^{(s)}(x_i, x_s) = \psi_i + \frac{1}{m} \int_0^\infty \left\{ P_i^{(s)} - \sum_{-T}^{(s)} P_i \right\} d\tau \quad (12)$$

$Q_i^{(s)}$ is the position the i-th particle in the s-tuple collision at time zero would have had if the particle had gone on with the initial momentum $P_i^{(s)}$. With the definitions (11) and (12), one has therefore:

$$F_s^{(0)}(x_1, \dots, x_s; F_i) = \prod_{i=1}^s F_i(Q_i^{(s)}, P_i^{(s)})$$

and according to (4b) this leads to :

$$A_i(x_1, F_i) = \int dx_2 \left\{ \Phi_{1,2} F_1(Q_1^{(2)}, P_1^{(2)}) F_2(Q_2^{(2)}, P_2^{(2)}) \right\} \quad (14)$$

We will show the relation of this expression to the Boltzmann collision operator presently. However, let us first look at the :

Second approximation.

To determine $F_s^{(1)}$ ($s \geq 2$), one has from (5b) :

$$D_0 F_s^{(1)}(x_1, \dots, x_s; F_1) = \{H_s, F_s^{(1)}\} + \Psi_s(x_1, \dots, x_s; F_1), \quad (15)$$

where we have put

$$\Psi_s \equiv -D_0 F_s^{(0)} + \int dx_{s+1} \left\{ \sum_{i=1}^s \phi_{i,s+1} F_{s+1}^{(0)} \right\}. \quad (16)$$

Clearly Ψ_s is known. In fact from the definition (6) of D , one gets :

$$\begin{aligned} \Psi_s(x_1, \dots, x_s; F_1) = & - \sum_{i=1}^s A_i(Q_i^{(s)}, P_i^{(s)}; F_1) \prod_{j=1}^i F_j(Q_j^{(s)}, P_j^{(s)}) \\ & - \int dx_{s+1} \left\{ \sum_{i=1}^s \phi_{i,s+1} \prod_{j=1}^{s+1} F_j(Q_j^{(s+1)}, P_j^{(s+1)}) \right\} \end{aligned} \quad (16a)$$

Now put in (15) $S_{-\tau}^{(1)} F_1$ for F_1 again; then one gets

$$\frac{\partial}{\partial \tau} F_s^{(1)}(x_1, \dots, x_s; S_{-\tau}^{(1)} F_1) = \{H_s, F_s^{(1)}\} + \Psi_s(x_1, \dots, x_s; S_{-\tau}^{(1)} F_1).$$

Using now the complete solution (10), one gets :

$$\begin{aligned} F_s^{(1)}(x_1, \dots, x_s; S_{-\tau}^{(1)} F_1) = & S_{-\tau}^{(1)} F_s^{(1)}(x_1, \dots, x_s; F_1) + \\ & + \int_0^{\tau} d\tau' S_{(\tau-\tau')}^{(1)} \Psi_s(x_1, \dots, x_s; S_{-\tau'}^{(1)} F_1), \end{aligned}$$

or (also changing $\tau - \tau'$ to τ') :

$$\begin{aligned} F_s^{(1)}(x_1, \dots, x_s; F_1) = & S_{-\tau}^{(1)} F_s^{(1)}(x_1, \dots, x_s; S_{\tau}^{(1)} F_1) + \\ & + \int_0^{\tau} d\tau' S_{-\tau'}^{(1)} \Psi_s(x_1, \dots, x_s; S_{\tau'}^{(1)} F_1) \end{aligned}$$

The left-hand side is again independent of τ , so by going to the limit $\tau \rightarrow \infty$, and using the boundary condition (7a), one gets :

$$F_s^{(1)}(x_1, \dots, x_s; F_1) = \int_0^{\infty} d\tau S_{-\tau}^{(1)} \Psi_s(x_1, \dots, x_s; S_{\tau}^{(1)} F_1) \quad (17)$$

which inserted in (4) gives for the triple collision term in the basic

kinetic equation (1) :

$$A_1(x_1; F_1) = \int dx_2 \left\{ \Phi_{1,2} \right\}_0 \int_0^\infty d\tau S_{-\tau}^{(2)} \Psi_2(x_1, x_2; S_{-\tau}^{(1)} F_1) \} \quad (18)$$

It is now clear how the successive approximation method clicks along.

25. The Boltzmann equation.

We conclude with Bogolubov's proof of the equivalence of the expression (14) for $A_1(x_1; F_1)$ with the Boltzmann collision operator. This equivalence is only rigorously true for the case where F_1 depends only on the impulse. In this case we will write $w(t, p)$ for $F_1(t, x)$. Of course in this case $A_0(x; F_1) = \{ T(p), w(t, p) \} = 0$. Now note that in general

$$\{ H_s(x_1, \dots, x_s), f(P_1^{(s)}, \dots, P_s^{(s)}) \} = 0 \quad (19)$$

where f is an arbitrary function and the $P^{(s)}$ are defined by (11). The proof follows by observing that the Poisson bracket (19) must have the same form whether expressed in the variables x_1, \dots, x_s or in the variables $S_{-\tau}^{(s)} x_i$, because the transition from x_1 to $S_{-\tau}^{(s)} x_i$ is a contact transformation and the Poisson bracket is invariant under such transformations. But for $\tau \rightarrow +\infty$, H_s will not depend on the coordinates since the particles are then far apart, and the Poisson bracket of two functions of the momenta is zero; hence (19) follows.

Apply (19) for two particles with $H(x_1, x_2) = T(p_1) + T(p_2) + \Phi_{1,2}$ and $f(P_1^{(2)}, P_2^{(2)}) = w(t, P_1^{(2)}) = w(t, P_2^{(2)}) = F_2(x_1, x_2; F_1)$; then one gets from (14)

$$\begin{aligned} A_1(x_1; F_1) &= \int dx_2 \left\{ \Phi_{1,2}, w(t, P_1^{(2)}) w(t, P_2^{(2)}) \right\} \\ &= - \int dx_2 \left\{ T(p_1) + T(p_2), w(t, P_1^{(2)}) w(t, P_2^{(2)}) \right\} \\ &= \iint d\vec{q}_2 d\vec{p}_2 \left\{ \frac{P_2 \cdot x}{m} \frac{\partial}{\partial q_{2x}} + \frac{P_{2x}}{m} \frac{\partial}{\partial q_{2x}} \right\} w(t, P_1^{(2)}) w(t, P_2^{(2)}) \end{aligned}$$

Since $P_1^{(2)}$ and $P_2^{(2)}$ depend only on $|\vec{q}_2 - \vec{q}_1|$ (central forces!)

$\frac{\partial}{\partial q_{1x}} = - \frac{\partial}{\partial q_{2x}}$. Take cylindrical coordinates now for the dq_2 integration, with the origin in \vec{q}_1 and axis in the direction of the relative velocity $\frac{1}{m}(\vec{P}_2 - \vec{P}_1)$; call the coordinate along this axis ξ ; then :

$$\frac{P_1^{(2)} - P_1^{(1)}}{m} = \frac{\partial}{\partial q_{1x}} w(t, P_1^{(1)}) w(t, P_2^{(1)}) = \frac{|\vec{p}_1 - \vec{p}_2|}{m} \frac{\partial}{\partial \xi} w(t, P_1^{(1)}) w(t, P_2^{(1)})$$

One now can integrate over ξ . Remember that $P_1^{(2)}(x_1, x_2)$ and $P_2^{(2)}(x_1, x_2)$ are the impulses with which the two bodies start off in the collision which goes through the phase x_1, x_2 . Therefore

$$\left\{ P_1^{(1)}(x_1, x_2) \right\}_{\xi = -\infty} = P_1, \quad \left\{ P_2^{(1)}(x_1, x_2) \right\}_{\xi = -\infty} = P_2$$

and

$$\left\{ P_1^{(2)}(x_1, x_2) \right\}_{\xi = +\infty} = P_1^*, \quad \left\{ P_2^{(2)}(x_1, x_2) \right\}_{\xi = +\infty} = P_2^*$$

where P_1^*, P_2^* are the impulses of the "restituting collision" (P_1^*, P_2^*) (P_1, P_2). Since because of the axial symmetry $d q_2 = 2\pi b db d\xi$ (where b is the impact parameter), one gets :

$$A_1(x_1, F_1) = 2\pi \int d\vec{p}_2 \int_0^{\infty} b db \int_0^{\pi} w(t, P_1^*) w(t, P_2^*) - w(t, P_1) w(t, P_2) d\theta \quad (20)$$

with :

$$g = \frac{1}{m} |\vec{p}_2 - \vec{p}_1|, \quad 2\pi b db = 2\pi I(g, \theta) \sin \theta d\theta; \quad \text{so (20)}$$

is just the Boltzmann collision operator.

For the general case in which F_1 depends also on the coordinates, Eq. (14) is only equivalent to the Boltzmann collision operator if one neglects the difference in the positions of the two collision "partners" during a collision. Otherwise one gets correction terms (described by Bogolubov as a kind of "inter-ferece" between the streaming and the collision terms), which contribute to the equation of state (remember that the Boltzmann equation leads to the ideal gas law!) and also presumably to the μ , correction in the viscosity. For elastic spheres this was already noticed by Enskog (see Chapter 16 in Chapman and Cowling).

For the discussion of the hydrodynamical stage, I have to refer to the book

N. Bogolubov, Problemy Dinamicheskoi Teorii v Statisticheskoi Fizike

Addition to Ch. 9

An excerpt of the paper of Kac. Consider first.

a . Stationary, discrete stochastic series , which need not be Markoffian . We will extend the result of Ch. 7 for this more general case .

Denote by \tilde{n}_i " not n_i " , so that for instance :

$$W_1 (\tilde{n}_1) = 1 - \sum_j W (n_j)$$

$$W_2 (n_i, \tilde{n}_k) = \sum_{j \neq k} W_2 (n_i, n_j)$$

etc . Drop the index i , and choose a fixed value of n . Then, from the stationarity , and the general consistency relations between the successive distribution functions , one sees :

$$W_{k+2} (n, \underbrace{\tilde{n} \dots \tilde{n}}_k, n) = W_{k+1} (n, \underbrace{\tilde{n} \dots \tilde{n}}_k) - W_{k+2} (n, \underbrace{\tilde{n} \dots \tilde{n}}_{k+1}) \quad (a)$$

$$W_{k+1} (n, \underbrace{\tilde{n} \dots \tilde{n}}_k) = W_k (\underbrace{\tilde{n} \dots \tilde{n}}_k) - W_{k+1} (\underbrace{\tilde{n} \dots \tilde{n}}_{k+1}) \quad (b)$$

$$W_{k+2} (n, \underbrace{\tilde{n} \dots \tilde{n}}_{k+1}) = W_{k+1} (\underbrace{\tilde{n} \dots \tilde{n}}_{k+1}) - W_{k+2} (\underbrace{\tilde{n} \dots \tilde{n}}_{k+2}) \quad (c)$$

Calling for abbreviation :

$$w_s = W_s (\underbrace{\tilde{n} \dots \tilde{n}}_s)$$

one gets by combining (a), (b) and (c), the basic lemma :

$$W_{k+2}(n, \tilde{n}, \dots, \tilde{n}, n) = w_k - 2w_{k+1} + w_{k+2} \quad (1)$$

For $k = 0$, (a) and (c) are still valid ; (b) becomes :

$$W_1(n) = W_0(\tilde{n}) - W_1(\tilde{n})$$

also true if $W_0 = 1$. So (1) remains valid for $k = 0$.

Theorem 1_a : For each n :

$$\sum_{k=0}^{\infty} P_{k+2}(n | \tilde{n}, \dots, \tilde{n}, n) = 1 \quad (2)$$

Proof : The conditional probability P_{k+2} is defined by :

$$P_{k+2}(n | \tilde{n}, \dots, \tilde{n}, n) = \frac{W_{k+2}(n; \tilde{n}, \dots, \tilde{n}; n)}{W_1(n)}$$

From (1) one gets easily :

$$\sum_{k=0}^N W_{k+2}(n, \tilde{n}, \dots, \tilde{n}, n) = 1 - W_1(\tilde{n}) + w_{N+2} - w_{N+1}$$

Now $w_{N+1} \gg w_{N+2}$, since $N+2$ successive \tilde{n} -values must be less probable than $N+1$ values, and the w 's are not negative and bounded, so $\lim_{N \rightarrow \infty} w_N$ exists, and therefore $\lim_{N \rightarrow \infty} (w_{N+2} - w_{N+1}) = 0$, from which (2) follows.

Eq. (2) is the Wiederkkehr theorem for discrete stochastic series.

It says, that it is certain that an n -value will come back after some time $k \sim$.

Theorem 2. . If : $\lim_{N \rightarrow \infty} w_N (\tilde{n} \dots \tilde{n}) = 0$ (3)

then the average recurrence time of the state n is given by :

$$\tau(n) = \frac{\tau}{w_1(n)} \quad (4)$$

Proof : Since by definition :

$$\tau(n) = \sum_{k=0}^{\infty} (k+1) \tau P_{k+2} (n / \tilde{n} \dots \tilde{n}, n)$$

one has to show :

$$\sum_{k=0}^{\infty} (k+1) w_{k+2} (n, \tilde{n} \dots \tilde{n}, n) = 1$$

From (1) one gets easily :

$$\sum_{k=0}^{N-1} w_{k+2} (n, \tilde{n} \dots \tilde{n}, n) = 1 - \{N (w_N - w_{N+1}) + w_N\}$$

Now , since the left side is a non decreasing sequence , $N (w_N - w_{N+1}) + w_N$ forms a non increasing sequence of positive terms, so that the limit for $N \rightarrow \infty$ exists . Since $\lim w_N$ exists according to (3) , $\lim N (w_N - w_{N+1})$ exists . Now, the series of non negative terms $\sum (w_N - w_{N+1})$ converges

$$\left[\sum_{N=0}^M (w_N - w_{N+1}) = 1 - w_{M+1} , \text{ and } \lim_{M \rightarrow \infty} w_{M+1} = 0 \right] , \text{ and therefore}$$

if the limit of $N (w_N - w_{N+1})$ exists (and we know that it does) the limit must be zero . This completes the proof . Consider now :

b. The streaming in Γ -space , say between two energy surfaces

E and $E + \Delta E$. Call the total volume $\Omega = 1$, and let A be a small region . (We will speak about a region, by which we mean the small

cylindrical volume between the two energy surfaces) . Let T be a volume preserving transformation of the Γ' -space into itself ; say T is the streaming of the ensemble fluid in the time τ . Successive transformations will be denoted by T^n . One then has :

Theorem 1_b . (Poincaré's theorem) : For almost all points ω in A there exists an $n \geq 1$, such that $T^n \omega$ is again in A .

Proof : Let $f(\omega)$ be the characteristic function of the region A (which means : $f(\omega) = 1$ if ω is in A , and zero otherwise) . The sequence : $f(\omega), f(T\omega), f(T^2\omega) \dots$ can be considered as a discrete, stationary stochastic series . Each variable can have the values one or zero with probability $[A]$ and $1 - [A]$, if $[A]$ is the volume of A . $W_{k+2}(1, \underbrace{0 \dots 0}_k, 1)$ is the volume of those points in A which after $k+1$ steps return to A . Theorem 1_a applies , and the statement $\lim_{k \rightarrow \infty} \frac{W_{k+2}(1, 0 \dots 0, 1)}{W_1} = [A]$ means that the total volume of points ω which eventually will return to A is equal to the volume of A , so that almost all points will return (" almost " because a set of points of measure zero may be an exception)

Theorem 2_b . If T is metrically transitive (or if the motion is ergodic) , and if $n(\omega)$ is the first $n \geq 1$ for which , if ω is in A , $T^n \omega$ is again in A , then :

$$\int_A n(\omega) d\tau = 1$$

or the ensemble average of the length of the Poincaré cycles :

$$\Theta = \frac{1}{[A]} \int_A n(\omega) d\tau = [A]$$

which is analogous to 4

Proof : One has to show that the metrical transitivity implies condition 3 . Now condition (3) is in the dynamical case

$$\lim_{n \rightarrow \infty} \int_{\Omega} d\omega \prod_{k=0}^n (1 - f(T^k \omega)) = 0 \quad (5)$$

which means that the volume of the points in Ω which are never reached by any point in A is zero . Clearly this will be the case if the motion is ergodic . According to the ^{it} Kirchoff ergodic theorem implies that the time average of any function of the motion is equal to the ensemble average . Therefore especially , for any point ω in Ω :

$$\lim_{n \rightarrow \infty} \frac{1}{n} \sum_{k=1}^n f(T^k \omega) = [A] \quad (6)$$

Let B be the set of points , which is never reached by any point in A .

So , if a point ω is in B $f(T^k \omega) = 0$ and therefore

$\lim_{n \rightarrow \infty} \frac{1}{n} \sum_{k=1}^n f(T^k \omega) = 0$; so B must have measure zero, since we know from (6) that for all ω (except for a possible set of measure zero) the limit is $[A]$.

Additions to Ch. 18 and 19 .

I. - The Chapman - Enskog theory is limited because of the following three basic assumptions which have been made :

a - Central forces , which limits the theory to mono-atomic gases .

b - Small value of the development parameter $L \frac{V(\text{macr. qu.})}{\text{macr. qu.}}$, which limits the theory to slowly varying phenomena (no shock waves , or very high frequency sound , where the wavelength becomes comparable with L). Also Knudsen gases, where L is comparable with macroscopic dimensions , can not be treated .

c - Binary collisions , which limits the theory to gases of low density . This last restriction is the most difficult to remove , since one has to extend the Boltzmann equation in a fundamental and still Bogolubov unknown way . It is dealt with in the last part of the notes .

2 . - The extension to poly atomic gases . The interest lies especially in the application to the propagation of sound . Already in 1881 Lorentz remarked that for polyatomic one must expect besides the viscosity and heatconduction coefficients μ and η , a third gas constant connected with the transfer of translational energy to internal energy , and that this should have some effect on the propagation of sound . For low frequency where the equilibrium between translational and internal degrees of freedom has time to adjust itself all the time , the velocity of sound will be given by the classical formula :

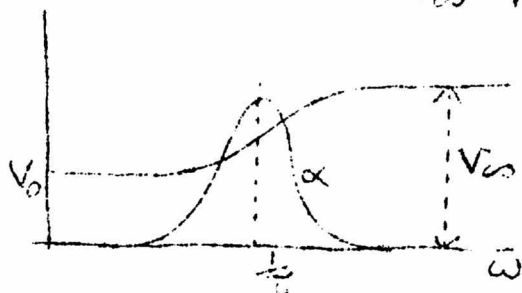
$$v_0 = \sqrt{\frac{C_p}{C_v} \frac{k T}{m}}$$

If we assume however that the transfer of energy needs on the average a time τ , so that one has an equation of the form :

$$\frac{d U_{\text{int}}}{dt} = \frac{U_{\text{transl.}} - U_{\text{int.}}}{\tau} \quad (1)$$

(analogous to Newton's law of cooling), then for frequencies $\omega \gg \frac{1}{\tau}$, the internal energy U_{int} will remain unaffected, and the gas will behave as a mono-atomic gas, so that:

$$V_{\infty} = \sqrt{\frac{5}{3} \frac{kT}{m}}$$



One gets a dispersion region around $\frac{1}{\tau}$ accompanied with an absorption α .

This effect was actually discovered by Kneser in the late twenties for CO_2 , and since the theory has been considered by various authors (Rutgers, Herzfeld- Rice, Bourgin, Landau- Teller a . 0) See the review of W.T.Richards, Rev. of Mod.Ph.II, 36 (1939). There remained the task to incorporate these developments into the general Chapman-Enskog theory. Already in 1922 this was tried by Pidduck (see Chapman and Cowling, Ch.11). Pidduck assumed that the molecules were rough elastic spheres, so that in a collision translational energy could be transformed into rotational energy. For this model the Chapman-Enskog theory can be generalized, but the model is so artificial that it is hard to see what it has to do with reality. Furthermore, the dispersion of sound is usually caused by the difficulty of the transfer of translational into vibrational energy, and only recently the so-called rotational sound dispersion has been observed for hydrogen.

The origin of the difficulty to extend the theory to more realistic

molecular models lies in the fact that in the classical theory with non-spherical molecules the probabilities for the direct and restituting collisions are in general not equal to each other . It is well known that this fact (also first pointed out by Lorentz) already causes difficulties in the proof of the Maxwell-Boltzmann distribution . It forced Boltzmann to generalize his proof of the H-theorem by considering cycles of collisions (see last chapter of Vol. II in the Gas theorie of Boltzmann) . Dr. C.S. Wang Chang and myself have evaded this difficulty by describing the internal degrees of freedom of the molecule quantum mechanically .⁽¹⁾ Instead of one distribution function f , we now describe the state of the gas by a series of distribution functions :

$$f_i \equiv f(\vec{r}, \vec{\xi}, E_i, t)$$

giving the number of molecules in the phase-cell $d\vec{r} d\vec{\xi}$ which are in the i^{th} quantum state with internal energy E_i . The Boltzmann equation becomes:

$$\frac{D f_i}{D t} = \sum_{j,k\rho} \int d\vec{\xi}_1 \int d\Omega g \int_{ij}^k I^{k\rho}(\mathbf{g}, \theta, \varphi) [f'_k f'_{\rho} - f_i f_{ij}] \quad (2)$$

The $\int_{ij}^k I^{k\rho}(\mathbf{g}, \theta, \varphi)$ is the differential collision cross-section for a collision of two molecules in the states E_i and E_j , where after collision they are in the states E_k , E_{ρ} and where the relative velocity has turned over the angles θ, φ , in the solid angle $d\Omega$. The magnitude of the relative velocity changes in general too (because of conservation of energy) , say to g' ! However the principle of microscopic reversibility

remains valid, so that :

$$g \int_{ij}^{kl} = g' \int_{kl}^{ij} \quad (3)$$

This relation is the reason why the semi quantum theoretical description is so much simpler than the classical description. Finally in (2)

$f_{ij} \equiv f(\vec{r}, \vec{\xi}, E_j, t)$ and f'_k, f'_ℓ are defined analogously.

Especially for the application to the propagation of sound it is convenient to distinguish the two limiting cases :

a - The inelastic collision cross section is of the same order of magnitude as the elastic cross section.

b - $I_{inelast} \ll I_{elast}$.

and to arrange the successive approximations in these two cases differently.

We begin with :

a . Transfer of translational to internal energy goes easy .

The treatment is then very similar to the mono-atomic case. In zeroth approximation, one starts from the complete, local equilibrium distribution:

$$f_i^{(0)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{1}{\sum_s \exp(-E_s/kT)} \exp \left[-\frac{1}{kT} \left\{ \frac{1}{2} m (\vec{\xi} - \vec{u})^2 + E_i \right\} \right]$$

dependent on the five macroscopic quantities n, \vec{u} , and T , which are still functions of x, y, z and t . In this approximation one again gets the Euler equations, only now the thermal energy Q depends more complicatedly on T , since the internal specific heat C_{int} is in general temperature dependent.

In first approximation one also gets the Navier-Stokes equations

but now :

$$\left. \begin{aligned} P_{ij} &= p \delta_{ij} - 2\mu \left(D_{ij} - \frac{1}{3} D_{\alpha\alpha} \delta_{ij} \right) - \kappa \delta_{ij} D_{\alpha\alpha} \\ q_i &= - (\lambda_{tr} + \lambda_{int.}) \frac{\partial T}{\partial x_i} \end{aligned} \right\} \quad (4)$$

The only differences with the case of the mono-atomic gas are, that the heat conductivity consists of two parts, and that, as Lorentz said, a new constant, the so-called dilatational viscosity coefficient κ appears. The constants λ_{tr} , λ_{int} , and κ can be expressed in the I_{ij}^k , which are supposed to be known. They can be in principle calculated if the molecular model and the interaction law are known, although in practice this is usually a very difficult task. As example I only give the expression for κ :

$$\kappa = \left(\frac{c_{int}}{c_{tot}} \right)^2 \frac{1}{2} \sqrt{\pi m k T} \frac{\left(\sum_i e^{-\epsilon_i} \right)^2}{\sum_{ijkl} e^{-\epsilon_i - \epsilon_j} \iint d\Omega dG (\Delta\epsilon)^2 G^3 e^{-G^2} I_{ij}^k} \quad (5)$$

where $\epsilon_i = E_i/kT$ and $\Delta\epsilon = \epsilon_k + \epsilon_l - \epsilon_i - \epsilon_j$. Because of the factor $(\Delta\epsilon)^2$ clearly only the inelastic collisions give a contribution to κ .

Applied to the propagation of sound, in the validity of this first or Navier-Stokes approximation, one does not get any dispersion of the sound. The dilatational viscosity only gives a contribution to the classical (Kirchoff) or " ω^2 " absorption. One finds for the absorption coefficient :

$$\frac{\omega^2}{\rho v_0^3} \left\{ \left(\frac{4}{3} \mu + \kappa \right) + \frac{mk}{c_p c_v} \lambda \right\} \quad (6)$$

The effect of \mathcal{K} can therefore not be separated from the classical causes of sound absorption through the viscosity and the heat conduction .

b - Transfer of translational to internal energy is difficult .

In this case, it can occur easily that in perturbations of the equilibrium state the temperature of the translational motion differs from the temperature of the internal degrees of freedom . It is therefore better to describe the state of the gas by six instead of five macroscopic quantities , namely

ρ , u_i , $T_{\text{transl.}}$ and $T_{\text{int.}}$. By taking the inelastic collisions into account in a one higher approximation than before, one gets in zeroth approximation again the Euler equations together with $DT_{\text{int.}}/DT = 0$. In first approximation however one does not get the Navies-Stokes equations , but the equations first put forward by Herzfeld and Rice (Phys. Rev. 31 , 691 , 1928) on phenemenological grounds . One obtains , besides the continuity equation and the equation of motion (in which the pressure tensor has now the same form as for a mono-atomic gas , therefore without a dilatational viscosity term), two energy equations , which determine the changes of $T_{\text{tr.}}$ and $T_{\text{int.}}$. The really new equation is :

$$c_{\text{int.}} \frac{\partial T_{\text{int.}}}{\partial t} = \frac{m \lambda_{\text{int}}}{\rho} \Delta T_{\text{int.}} + \frac{c_{\text{int.}}}{\tau} (T_{\text{tr.}} - T_{\text{int.}}) \quad (7.)$$

The physical interpretation is clear . There are again four gas constants $\lambda_{\text{tr.}}$, $\lambda_{\text{int.}}$, μ and τ , which can be expressed in I_{ij}^k . In the $\lambda_{\text{tr.}}$ and μ occurs now only the elastic collision cross-section, so that just as in the mono-atomic case one has with good approximation :

$$\lambda_{\text{tr.}} = \frac{5}{2} \mu c_{\text{tr.}}$$

In the relaxation time τ occurs only the inelastic collision cross-section, and the expression for τ is very analogous to the expression (5) for κ . Formally in fact:

$$\kappa = \frac{c^3_{int.}}{c^2_{tot.}} n k T \quad (8)$$

Applied to the propagation of sound (as done already by Herzfeld and Rice) one gets a dispersion region around the frequency ω , accompanied by an absorption band, which is well separated from the " " absorption region caused by the viscosity and heat conduction, for which one gets eq.(6) with $k = 0$.

II - Extension to fast varying phenomena. The question is, what to do when the Chapman-Enskog development parameter: $\frac{\nabla(\text{macr. qu})}{\text{macr. qu.}}$ is not more small, as will be the case for Knudsen gases, and for fast varying phenomena (structure of shock waves, propagation of high frequency sound). Of special interest are the experiments of Greenspan (J. Acoust. Soc. 22, 56 (1950) on the dispersion and absorption of high frequency (up to 1 mH) sound in Helium at low pressures (about 0.1 mm of Hg.). Greenspan plots his result as function of the dimensionless parameter $G = \frac{\mu \omega}{\rho \cdot V_0^2}$, which is $\sim \frac{\omega}{\omega_{coll}}$, where the collision frequency $\omega_{coll} \sim \frac{1}{V} \left[\frac{\rho \cdot V_0^2}{\mu} \right]$ For Maxwell molecules, with L the transport mean free path, one gets $G = \frac{3\pi}{2} \frac{\omega}{\omega_{coll}}$. Biggest value of G is about 10, so one really has extreme conditions. For $G = 10$, the velocity has increased to about $3 V_0$, while for $G=2$ the absorption coefficient is already 0.5, so that the intensity drops by

a factor $1/e$ in 2 cm .

a. One can try to extend the theory by carrying the development further. It is to be noted that the successive order hydrodynamical equations (Euler, Navier-Stokes, Burnett, etc) are all of the first order in the time derivatives of the macroscopic quantities ρ, u_i and T , and are of successive order in the space derivatives . Therefore to solve the initial value problem it is always sufficient to give the initial values of ρ, u_i and T . This fact is called the macroscopic causality theorem (Hilbert) . It is paradoxical because from the Boltzmann equation it would appear that one would need the initial value of the whole distribution f , which is much more than the first five moments (in the velocity) ρ, u_i and T . One must say the causality theorem is not a theorem but an " Ansatz " . Starting from an arbitrary initial velocity distribution one must assume that in a short time (of order L / \bar{v}) the gas reaches a " normal " state, from which the further temporal development proceeds according to the macroscopic causality theorem (Compare the hydrodynamical stage in the Bogolubov theory , Ch. 23) .

b. There are few practical applications of the Burnett equations . The propagation of sound has been considered by Primakoff and by C.S. Wang Chang . The result can be found simpler in an other way , which we will discuss in a moment . It is clear anyway , that as soon as the parameter $L \frac{\nabla(\text{macr.qu.})}{\text{macr.qu.}}$ is comparable with one, the Chapman-Enskog development will be of little use .

c. It is good to remember a remark made by Osborne Reynolds . One knows

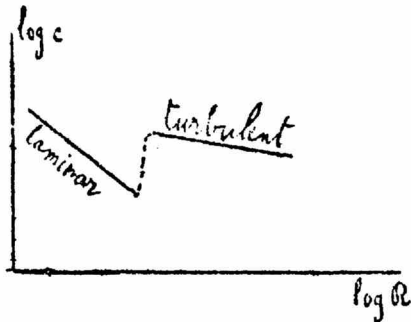
that for viscous and incompressible fluids all dimensionless numbers (of drag, lift , etc) can only be function of the Reynolds number R . For instance for the flow through a circular tube the resistance coefficient C , defined by :

$$P_1 - P_2 = C \frac{L}{R} \frac{\rho V^2}{2}$$

(P_1, P_2 are the pressures at the ends of the tube of length L , radius R ; ρ, V are density and average velocity of the fluid) is a function of

$$R = \frac{\rho V R}{\mu}$$

if μ = viscosity coefficient . The function $C (R)$ summarizes all the experiments about the flow ; for low speed one has (Poiseuille)



$$C (R) = \frac{16}{R}$$

while for large R one gets the turbulent regime with a different law for C .

Now, from the kinetic theory for a gas

$$\mu \sim \rho L v$$

if v is an average molecular velocity . Therefore :

$$R \sim \frac{V}{v} \cdot \frac{R}{L}$$

is really the product of two dimensionless numbers . Only if $V/v \ll 1$ and $R/L \gg 1$ will they enter the theory as the product .

In general (at high speeds , or for low pressures (Knudsen gas) one must expect that both numbers will enter independent of each other . We will call L/R the Knudsen number ; since the sound velocity is of same

order as the average molecular velocity \sqrt{v} can be taken as the Mach number .

d. In general, one can say that in any non equilibrium situation one can distinguish between :

1. The magnitude of the disturbance from equilibrium , and measured by a " Mach " number, and 2 the scale of the disturbance from equilibrium , which is measured by the Knudsen number . Examples : a propagation of sound, magnitude of the disturbance is determined by the intensity , the scale by the wave length of the sound ; b motion of a sphere through a gas, magnitude of disturbance is determined by the speed (measured by the usual Mach number) , the scale by the size of the sphere comp. to the mean free path ; c heatflux between two parallel plates with temperatures T_1 and T_2 ; magnitude of disturbance is determined by the " Mach" number $(T_2 - T_1) / \frac{1}{2} (T_1 + T_2)$, the scale by the Knudsen number L / d , if $d =$ distance between plates .

It seems to me unlikely , that there exist macroscopic equations , which would be valid for all values of both the Mach and the Knudsen number . It also seems better to make developments in either the Mach or in the Knudsen number , and not in the combination M / K as is done in the Chapman-Enskog development .

e . For all disturbances , one can always write :

$$f = f_0 (1 + h (\vec{r}, \vec{v}) t)$$

where f_0 is the complete (therefore not the local) equilibrium

distribution and h is the disturbance. If $h \ll 1$, one gets the homogeneous equation :

$$\sqrt{\frac{m}{2kT}} \frac{\partial h}{\partial t} + c \frac{\partial h}{\partial x} = n \mathcal{I}(h) \quad (1)$$

with :

$$\mathcal{I}(h) = \frac{1}{\pi^{3/2}} \int d\vec{c}_1 e^{-c_1^2} \int d\Omega g \mathcal{I}(g, \theta) (1 + h'_1 - h - h_1)$$

is the linearized collision operator, and where we use again the dimensionless velocity $c_i = \sqrt{\frac{m}{2kT}} \cdot \xi_i$. No assumption is made about the scale of the disturbance.

For example, for the propagation of sound of low intensity but arbitrary wavelength one has to solve (1), if h has the form :

$$h(\vec{c}) = e^{i(\omega t - \sigma z)}$$

with ω real and $\sigma = \sigma_1 - i\sigma_2$. Developing $h(\vec{c})$ in the eigenfunctions of $\mathcal{I}(h)$:

$$h = \sum_{r \ell} a_{r \ell} \psi_{r \ell}(\vec{c})$$

(1) becomes the infinite system of linear homogeneous equations :

$$i \sqrt{\frac{m}{2kT}} \omega a_{r \ell} - i \sigma \sum_{r' \ell'} M_{r \ell; r' \ell'} a_{r' \ell'} = n \lambda_{r \ell} a_{r \ell} \quad (2)$$

where :

$$M_{r \ell; r' \ell'} = \int d\vec{c} c_z \psi_{r \ell} \psi_{r' \ell'}$$

is the matrix element of c_z and $\lambda_{r \ell}$ are the eigenvalues of $\mathcal{I}(h)$. For Maxwell molecules, the $\psi_{r \ell}$, $\lambda_{r \ell}$ are known (see Ch. 3) and the $M_{r \ell; r' \ell'}$ can easily be evaluated. The condition of solubility of the set (2) is that

the determinant :

$$\left| \left(i\omega\sqrt{\frac{m}{2kT}} - n\lambda_{rl} \right) \delta_{r'l,r'l} e^{-i\sigma M_{r'l,r'l}} \right| = 0 \quad (3)$$

which gives a relation between ω and σ , which is the dispersion law of the gas. One finds (always for Maxwell molecules, force law k/r^5 , using dimension less frequency $\omega_0 = \omega / n\sqrt{\frac{2k}{m}}$ and propagation constant

$$\sigma_0 = \sqrt{\frac{kT}{k}} \cdot \frac{\sigma}{n} \quad \text{for the beginning of the infinite determinant (3) :}$$

$2r+l$	l	0	1	2	3
0	0	ω_0	$\frac{1}{\sqrt{2}}\sigma_0$	0	0
1	1	$-\frac{1}{\sqrt{2}}\sigma_0$	ω_0	$\frac{1}{\sqrt{3}}\sigma_0$	$-\frac{\sqrt{2}}{\sqrt{3}}\sigma_0$
2	0	0	$\frac{1}{\sqrt{3}}\sigma_0$	ω_0	0
2	1	0	$\frac{1}{\sqrt{3}}\sigma_0$	ω_0	0
2	2	0	$-\frac{\sqrt{3}}{3}\sigma_0$	0	$\omega_0 + i\lambda_{02}$
3	1	0	0	$\frac{\sqrt{5}}{6}\sigma_0$	$\frac{2}{\sqrt{15}}\sigma_0$
3	2	0	0	0	$\omega_0 + i\lambda_{11}$
3	3	0	0	0	$-\frac{3}{\sqrt{10}}\sigma_0$
3	0	0	0	0	$\omega_0 + i\lambda_{03}$

We were only able to go further by using a breaking - off procedure, in which we were guided by the Chapman-Enskog development. We used successively

3x3, 5x5, 8x8, 11x11 terms . At each stage one has an algebraic relation between ω_0 and σ_0 . One can then treat these relations in two different ways . The first and really consistent way is to develop

$\sigma_0 = \sigma_{01} - i\sigma_{02}$ as a function of ω in powers of ω , which amounts to a development in powers of the Greenspan parameter G . In each approximation one retains those powers of G of which the coefficients are not changed in the next approximation . One thus gets :

$$\sigma_1 = \frac{\omega}{V} = \frac{\omega}{V_0} \left[1 - \frac{215}{72} G^2 + \frac{4,115,101}{27,34.7} G^4 - \dots \right]$$

" " " "

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$$\sigma_2 = \frac{\omega}{V_0} G \left[\frac{7}{6} - \frac{5155}{432} G^2 + 310.5 G^4 - \dots \right]$$

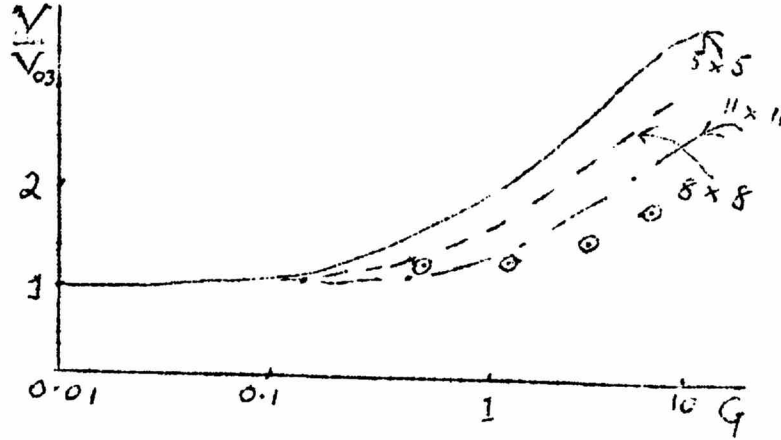
" " " "

11.9

These series are the same as obtained from the successive order hydrodynamical equations , but the derivation is much simpler . Because of the expected slow convergence they are of little use for the comparison with Greenspan's experiments .

The second and less consistent way is to solve in each approximation σ as function of ω exactly and compare the successive curves with experiment .

With the 11 x 11 determinant one then gets approximate agreement with experiment (see figure ; \odot are the experimental points .) However



since one has no idea about the convergence of the procedure, this agreement may not mean anything .

- ADDITION TO CH.22 .

From the Born-Green-Kirkwood- Yvon - Bogolubov hierarchy of equations (15) it is possible to derive general hydrodynamic equations , analogous to but more general than Eqs. (3), Ch.17 . Especially from the first equation (15a) of the hierarchy follows (if one includes outside forces) almost immediately the continuity equation :

$$\frac{\partial \rho}{\partial t} + \text{div} (\rho \vec{u}) = 0 \quad (1)$$

$$\rho = mn = m N \int F_1 (p, q) d \vec{p}$$

$$u_i = \frac{1}{n} \int \frac{p_i}{m} F_1 (p, q) d \vec{p}$$

and the equation of motion :

$$\rho \frac{D u_i}{D t} = \rho X_i - \frac{\partial P_{ij}}{\partial q_j} - \int d \vec{q} \frac{\partial \phi (\vec{q} - \vec{q}_1)}{\partial q_i} n_2 (\vec{q}, \vec{q}_1) \quad (2)$$

with

$$P_{ij} = \rho \overline{u_i u_j} = \text{kinetic stress tensor and :}$$

$$n_2(\vec{q}, \vec{Q}) = \frac{N^2}{2} \iint dp dR^2 P_2(q, p; Q, P)$$

is the pair density distribution. It is possible to write the last term in (2) as the divergence of the symmetric tensor :

$$P'_{ij} = \frac{1}{2} \int_0^\infty dR R^2 \frac{d\phi(R)}{dR} \iint d\vec{k} \int_0^R d\lambda k_i k_j n_2(\vec{q} + \vec{k}\lambda - \vec{k}R, \vec{q} + \vec{k}\lambda) \quad (3)$$

where \vec{k} is a unit vector pointing from \vec{q} to \vec{Q} . This was first pointed

out by Enskog. As a result one can combine the last two terms in (2) to

$\partial P_{i\alpha} / \partial q_\alpha$, where $P_{ij} = P_{ij} + P'_{ij}$ is the total stress tensor consisting of a kinetic and an intermolecular force part. The physical interpretation of (3) is clear. The formal proof is as follows :

Last term of (2) is of the form :

$$A_i = \int d\vec{Q} \cdot_i F(\vec{q}, \vec{Q})$$

where F is a scalar and symmetric function of \vec{q} and \vec{Q} . Now : $A_i = \frac{\partial S_{i\alpha}}{\partial q_\alpha}$

with :

$$S_{ij} = S_{ji} = \frac{1}{2} \int_0^\infty dR R^2 \iint d\vec{k} \int_0^R d\lambda k_i k_j F(\vec{q} + \vec{k}\lambda - \vec{k}R, \vec{q} + \vec{k}\lambda)$$

Proof : Verify :

$$\frac{\partial S_{i\alpha}}{\partial q_\alpha} = \frac{1}{2} \int_0^\infty dR R^2 \iint d\vec{k} \int_0^R d\lambda k_i k_\alpha \frac{\partial F}{\partial q_\alpha}$$

F is a function of $\vec{q} + \vec{k}\lambda$ and $\vec{k}R$, so that

$$\frac{\partial F}{\partial \lambda} = k_\alpha \frac{\partial F}{\partial q_\alpha}$$

Therefore :

$$\frac{\partial S_{iX}}{\partial q_\alpha} = \frac{1}{2} \int_0^\infty dR R^2 \iint d\vec{k} k_i \left\{ F(\vec{q}, \vec{q} + \vec{k}R) - F(\vec{q} - \vec{k}R, \vec{q}) \right\}$$

In the last integral, one interchanges the two points, which changes the direction of \vec{k} . Since F is symmetric one thus gets the same result as the first integral, so that :

$$\frac{\partial S_{iX}}{\partial q_\alpha} = \int_0^\infty dR R^2 \iint d\vec{k} k_i F(\vec{q}, \vec{q} + \vec{k}R)$$

which is just A_i [put origin of Q integration in \vec{q} , and use polar coordinates .]

In an analogous way, one can generalize the energy equation

(Comp . last of eqs. (3), Ch 17) to :

$$\rho \frac{D}{Dt} \left(\frac{Q}{\rho} + \bar{\phi} \right) + \text{div } \sigma_i = - P_{\alpha\beta} D_{\alpha\beta} \quad (4)$$

with $D_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial q_j} + \frac{\partial u_j}{\partial q_i} \right)$, P_{ij} = total stress tensor, and :
 $Q = \frac{1}{2} \rho \overline{u_\alpha u_\alpha}$ = density of the kinetic thermal energy .

$$\bar{\phi} = \frac{1}{n_2} \iiint \phi(\vec{q} - \vec{Q}) F_2(\vec{q}, \vec{p}; \vec{Q}, \vec{P}) d\vec{p} d\vec{P} d\vec{Q}$$

= potential energy density .

Finally, in (4) enters the total energy flux density σ_i , which just as the

P_{ij} consists of two parts : $\sigma_{ij} = q_j + q_i$

where $q_i = \frac{1}{2} \rho \overline{u_i u_\alpha u_\alpha}$ = kinetic thermal energy flux density, and

q'_i is the contribution due to the intermolecular forces. One finds :

$$q'_i = \frac{1}{2m} \int d\vec{Q} \frac{d\phi}{dR} \left[k_i k_\alpha \iint d\vec{p} d\vec{P} \int_0^R d\lambda (p_\alpha - \bar{p}_\alpha) F_2(\vec{q} + k\lambda - k\vec{R}, \vec{q} + k\lambda, P, P) + \frac{1}{2m} \int d\vec{Q} \phi(R) \iint d\vec{p} d\vec{P} (p_i - \bar{p}_i) F_2(q, p; Q, P) \right] \quad (5)$$

with $d\vec{Q} = R^2 dR d\vec{k}$. For the physical interpretation of (5) see Kirkwood.