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KINETIC THEORY OF RIGID MOLECULES.

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INTRODUCTION.

IT was shown by Boltzmann[1] that the behavior of a monatomic gas may be studied by means of the partial differential equation

$$\frac{\partial f}{\partial t}+\xi\frac{\partial f}{\partial x}+\eta\frac{\partial f}{\partial y}+\zeta\frac{\partial f}{\partial z}+X\frac{\partial f}{\partial \xi}+Y\frac{\partial f}{\partial \eta}+Z\frac{\partial f}{\partial \zeta}=J,$$

when the gas is an ensemble of the same kind of monatomic molecules. The f is the number of molecules per unit cell; the x, y, z; ξ, η, ζ; X, Y, Z are components of three dimensional space, velocity, and acceleration respectively and the J is the rate of change due to encounters. The obvious extension to any number of dimensions is

$$\frac{\partial f}{\partial t}+\Sigma\frac{\partial (f\dot{x}_i)}{\partial x_i}=J,$$

where the x's are any coördinates to specify the system of the individual molecule.

Now the deductions from this equation may be classified into two categories; namely, those which are independent of the form of J, and those which depend upon the nature of J. The hydrodynamic equations can be derived without knowledge of J, provided we admit the existence of such a function. On the other hand the quantitative determinations of the pressure, the viscosity, and the thermoconductivity can not be effected, unless we know something about J.

Since the form of J depends upon what is assumed concerning the nature and frequency of various types of encounters between the molecules it is convenient to classify the coördinates into two groups, according as they are or are not affected by encounters. Let us call the first, the

[1] Boltzmann, Gas Theorie, Vol. I., § 16.

affected coördinates, and the latter the immune coördinates. During encounters, if there is a function of the affected coördinates such that the sum of the function of the coördinates for one molecule and the same function of the coördinates for the other molecule remains unchanged, we shall call such a function an invariant of the encounter. Confining attention to binary encounters, if we have k affected coördinates of one molecule, then the question is to determine $2k$ variables after encounters in terms of $2k$ variables before encounter. If there are r invariants in this special sense in addition to the one purely numerical invariant, and s other general relations (without arbitrary parameters), then the equations of encounter will involve $2k - (r + s)$ parameters. Let Φ_i be the invariants of encounters including $\Phi_0 = 1$, then the equations $d\sigma_I \int \Phi_i J d\sigma_A = 0$; $i = 0 \cdots r$; will be valid and will give $r + 1$ fundamental equations of what may be called generalized hydrodynamics corresponding to the space of the immune coördinates. The $d\sigma_I$ is an element of the immune space and the $d\sigma_A$ is that of the affected space.

To illustrate the notion, let us consider the case of a monatomic gas.[1] The x, y, z are immune coördinates, and ξ, η, ζ are affected coördinates. The number, the three components of translational momentum, and the energy of the system are invariants of encounters, so that $r = 4$. For the parameters of an encounter, we have the longitude and latitude of the point of contact if we adopt the idea of an elastic sphere; the distance from the asymptotic line and the orienting angle if we choose the conception of central forces. Therefore $s = 0$, and consequently there are no additional relations entering into the consideration, and also there are no more invariants. The conservation of the number gives

$$\int J d\sigma_A = 0 \quad \text{(the numerical invariant).}$$

where $d\sigma_A = d\xi d\eta d\zeta$, which reduces to the equation of continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0,$$

where $\rho = \int m f d\sigma_A$, and $\mathbf{V}(V_x,\ V_y,\ V_z) = \mathbf{W}(\xi,\ \eta,\ \zeta) - \mathbf{U}(U_x,\ U_y,\ U_z)$.[2] The $\mathbf{V}$ is the mass velocity and $\mathbf{U}$ is the velocity of agitation.

The conservation of translational momentum gives

$$\int m \mathbf{W} J d\sigma_A = 0,$$

[1] Boltzmann, Gas Theorie, Vol. I. Maxwell, Collected Works, Vols. I. and II. Lorentz, Collected Works, Vol. II. Kirchhoff, Theoretische Physik, Vol. IV. Hilbert, Math. Annalen, Band 72, 1912, p. 562.

[2] In order to save space, Gibb's vector notation is used in this paper whenever it is convenient. The vectors are indicated by clarendon type.

which, when combined with the equation of continuity, reduces to the equation of motion in hydrodynamics,

$$\rho\left\{\frac{\partial \mathbf{V}}{\partial t}+\mathbf{V}\cdot\nabla\mathbf{V}\right\}+\nabla\cdot\Lambda-\rho\mathbf{g}=0,$$

where Λ is the dyadic of stress and g is the vector of acceleration. Finally the conservation of energy gives

$$\int m\frac{\mathbf{W}^2}{2}Jd\sigma_A=0,$$

which reduces, when combined with two preceding, to

$$\rho\left\{\frac{\partial e}{\partial t}+\mathbf{V}\cdot\nabla e\right\}+\nabla\cdot\mathbf{h}-\nabla\cdot(\Lambda\cdot\mathbf{V})-\mathbf{V}\cdot(\nabla\cdot\Lambda)=0,$$

where $\mathbf{h}$ is the flux vector of Fourier conduction of heat and e is the thermal energy per unit mass.

The present paper considers some features of the kinetic theory of gases under the assumption that the molecules are rigid bodies, having no spherical symmetry. The first part will deal with the general hydrodynamical relations. It is evident that we have to consider the orientation and the angular velocity[1] of each individual molecule besides its space coördinates and translational velocity. For invariants, we have three additional equations stating the conservation of moment of momentum. Then the space coördinates x, y, z and the angles φ, ψ, θ are regarded as immune coördinates so that the general idea explained above leads in the first place to a kind of hydrodynamics of six dimensions. The three angles of orientation are then integrated out so as to leave the suitably modified equations of ordinary hydrodynamics, together with an additional vector equation corresponding to the conservation of moment of momentum, which suggests the possibility of the propagation of gyroscopic disturbances besides the sound waves. It will be shown also in the second part that we can specify such binary encounters by five parameters. Consequently we have twelve variables, with seven invariants and five parameters of encounters, thus forming a complete system in the sense that all the independent invariants have been utilized.

The investigations of the specific heat of gases[2] from the standpoint of the equipartion of energy indicate that we can not treat gases like oxygen or hydrogen as monatomic. Thus we have to consider the energy of rotation, which is caused by asymmetry of shape and loading. The idea

[1] Tisserand, Méc. Céleste, Vol. II. Poisson, Méc., Vol. II. Appell, Méc. Rationelle, Vol. III.

[2] Kirchhoff, Theoretische Physik, Vol. IV., page 169. Jeans, Dynamical Theory of Gases, pages 81 and 171. Raleigh, Theory of Sound, Vol. II., page 18.

of considering gas molecules as rigid bodies was initiated by Maxwell,[1] who computed the impulse if two such bodies were to collide. Later various writers[2] carried out the work for some special cases. The second part of this paper will deal with a collision axiom for a more general type of rigid bodies, and some of its consequences. We shall discuss the distribution of translational and angular velocities, especially the equilibrium distribution and its relation to the H-theorem. The distribution function thus deduced will be utilized to compute the external pressures of such gas molecules.

I. Hydrodynamics.

Let x, y, z; ξ, η, ζ be the translational space and velocity coördinates. For orientational coördinates, we can use the Euler angles φ, ψ, θ; and angular velocities ω_1, ω_2, ω_3 (see Figs. 1 and 2). The system of moving

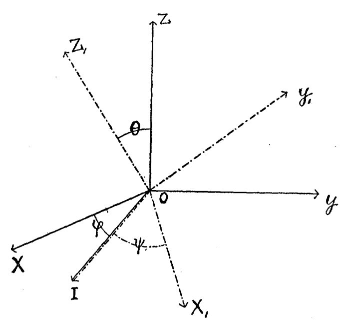

Fig. 1.

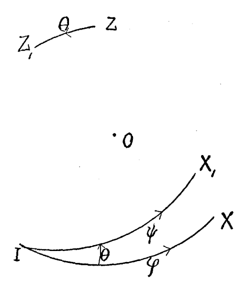

Fig. 2.

axes (x_1, y_1, z_1) and fixed axes (x, y, z) are connected by the following equations (if the translational motion is temporarily neglected).

$$x = lx_1 + my_1 + nz_1$$
$$y = l'x_1 + m'y_1 + n'z_1$$
$$z = l''x_1 + m''y_1 + n''z_1,$$

the nine direction cosines being expressed in terms of the Euler angles, as indicated in the following schema

$$\left\{\begin{matrix} l, & m, & n \\ l', & m', & n' \\ l'', & m'', & n'' \end{matrix}\right\} = \left\{\begin{matrix} \cos\varphi\cos\psi - \sin\varphi\sin\psi\cos\theta, \\ \qquad -\cos\varphi\sin\psi - \sin\varphi\cos\psi\cos\theta,\ \sin\theta\sin\varphi \\ \sin\varphi\cos\psi + \cos\varphi\sin\psi\cos\theta, \\ \qquad -\sin\varphi\sin\psi + \cos\varphi\cos\psi\cos\theta,\ -\sin\theta\cos\varphi \\ \sin\psi\sin\theta, \quad \cos\psi\sin\theta, \quad \cos\theta \end{matrix}\right\}.$$

[1] Maxwell: Collected Works, Vol. I., page 406.

[2] Jeans, Dynamical Theory of Gases, p. 93. Burbury, Phil. Trans., A CLXXXIII., p. 407, 1892. Burnside, Trans. R. S. E., XXXIII., part ii., 1887. N. Delone, Report of Russian Imp. University, 1892.

Then the three components of the angular velocities may be expressed in terms of the time derivatives[1] of the angles,

$$\omega_1 = \dot\varphi \sin\theta \sin\psi + \dot\theta \cos\psi,$$
$$\omega_2 = \varphi \sin\theta \cos\psi - \dot\theta \sin\psi,$$
$$\omega_3 = \dot\varphi \cos\theta \qquad + \dot\psi.$$

The auxiliary formulæ for the change of direction cosines may be obtained directly, thus

$$\dot l = m\omega_3 - n\omega_2, \quad \dot l' = m'\omega_3 - n'\omega_2, \quad \dot l'' = m''\omega_3 - n''\omega_2,$$
$$\dot m = n\omega_1 - l\omega_3, \quad \dot m' = n'\omega_1 - l'\omega_3, \quad \dot m'' = n''\omega_1 - l''\omega_3,$$
$$\dot n = l\omega_2 - m\omega_1, \quad \dot n' = l'\omega_2 - m'\omega_1, \quad \dot n'' = l''\omega_2 - m''\omega_1.$$

If the moving axes are chosen as the principal axes of the body, the dyadic of inertia is

$$\Gamma = Aii + Bjj + Ckk,$$

where A, B, C are the principal moments of inertia, and i, j, k are unit vectors along the moving axes.

Then the differential equations of the motion of a molecule are

$$\dot x = \xi, \quad y = \eta, \quad \dot z = \zeta,$$
$$\dot\xi = X, \quad \dot\eta = Y, \quad \dot\zeta = Z,$$

and

$$\dot\varphi = \frac{\sin\psi}{\sin\theta}\omega_1 + \frac{\cos\psi}{\sin\theta}\omega_2,$$
$$\dot\psi = \omega_3 - \cot\theta(\sin\psi\omega_1 + \cos\psi\omega_2),$$
$$\dot\theta = \cos\psi\omega_1 - \sin\psi\omega_2,$$
$$A\dot\omega_1 = (B - C)\omega_2\omega_3 + L,$$
$$B\omega_2 = (C - A)\omega_1\omega_3 + M,$$
$$C\dot\omega_3 = (A - B)\omega_1\omega_2 + N,$$

where X, Y, Z are the components of the impressed force, and L, M, N are the components of the impressed couple. The first specify the motion of the center of gravity, and the second specify the rotation of the body referred to the principal axes.

If f is the number of molecules per unit cell in the twelve dimensional region, and J is the rate of the change of this number of molecules due to encounters the Boltzmann equation may be written

$$J = \frac{\partial f}{\partial t} + \Sigma\frac{\partial(f\dot x)}{\partial x} + \Sigma\frac{\partial(f\dot\xi)}{\partial\xi} + \Sigma\frac{\partial(f\dot\varphi)}{\partial\varphi} + \Sigma\frac{\partial(f\dot\omega_1)}{\partial\omega_1}.$$

[1] The molecular time derivative is designated by placing a dot above the character, whereas the molar time derivative is designated by the ordinary form d/dt, $\partial/\partial t$.

Let us put for brevity

$$d\tau = dxdydz, \quad d\tau' = d\varphi d\psi d\theta,$$
$$d\sigma = d\xi d\eta d\zeta, \quad d\sigma' = d\omega_1 d\omega_2 d\omega_3.$$

The range of the variables will be

ξ	η	ζ ;	φ	ψ	θ;	ω_1	ω_2	ω_3 .
$-\infty$	$-\infty$	$-\infty$	0	0	0	$-\infty$	$-\infty$	$-\infty$
$+\infty$	$+\infty$	$+\infty$	2π	2π	π	$+\infty$	$+\infty$	$+\infty$

First let us deduce hydrodynamical relations in six dimensions. The conservation of the number gives

$$\int J d\sigma d\sigma' = 0.$$

Now define the density by the equation

$$\rho^* = \int mf d\sigma d\sigma'$$

so that

$$\frac{\partial \rho^*}{\partial t} = \int m \frac{\partial f}{\partial t} d\sigma d\sigma';$$

and also introduce the notation $\mathbf{W} = \mathbf{U} + \mathbf{V}$, where $\mathbf{W}$ is the velocity vector of the center of gravity of the molecule in question, its components being ξ, η, ζ; $\mathbf{V}$ is the vector of mass velocity, and $\mathbf{U}$ the vector of agitation velocity. It follows that $\int m\mathbf{U} f d\sigma d\sigma' = 0$. Then we have

$$m\int J d\sigma d\sigma' = \frac{\partial \rho^*}{\partial t} + \nabla \cdot (\rho^* \mathbf{V}) + \int_{\sigma^1} m \left\{ \Sigma X \int f d\eta d\zeta \right\} d\sigma'$$
$$+ \int m\Sigma \frac{\partial (f\dot{\varphi})}{\partial \varphi} d\sigma d\sigma' + \int_{\sigma} m \left\{ \Sigma \dot{\omega}_1 \int f d\omega_2 d\omega_3 \right\} d\sigma.$$

Further let us specify the nature of the external forces and torques, and the distribution function f in the following manner:

(1) Suppose X, Y, Z are independent of the velocities.

(2) Suppose L, M, N are independent of the angular velocities.

(3) Assume f to be such a function with respect to ξ's and ω's, that the surface integrals become zero as the surfaces extend to infinity.

Then the third and the fifth terms reduce to zero. Let us now write the fourth term as follows

$$\int m\Sigma \frac{\partial (f\dot{\varphi})}{\partial \varphi} d\sigma d\sigma' = \nabla_\phi \cdot (\rho^* \mathbf{N}^*),$$

where

$$\nabla_\phi \cdot = \left(i^* \frac{\partial}{\partial \varphi} + j^* \frac{\partial}{\partial \psi} + k^* \frac{\theta}{\partial \theta} \right).$$

and

$$\rho^*\mathbf{N}^* = \Sigma\int mf\dot{\varphi}d\sigma d\sigma'.$$

Also $\mathbf{N}^*$ is expressible as a linear combination of $\mathbf{M}^*$, where $\mathbf{M}^*$ is the vector of moment of momentum in the fixed space,

$$M_1^* = (ll''A + mm''B + nn''C)N_1^* + nCN_2^* + \cos\varphi N_3^*,$$

$$M_2^* = (l'l''A + m'm''B + n'n''C)N_1^* + n'CN_2^* + \sin\varphi N_3^*,$$

$$M_3^* = (l''^2A + m''^2B + n''^2C)N_1^* + n''CN_2^* + 0.$$

The symbol ∇_ϕ may be called angular divergence following the analogy of ordinary space. So finally we have

$$\frac{\partial\rho^*}{\partial t} + \nabla\cdot(\rho^*\mathbf{V}) + \nabla_\phi\cdot(\rho^*\mathbf{N}^*) = 0,$$

which is the equation of continuity in six dimensions.

The conservation of translational momentum, namely $\int m\mathbf{W}Jd\sigma d\sigma'$ may now be considered. If we define the dyadic of stress by

$$\int m\mathbf{UU}fd\sigma d\sigma' = \Lambda^*,$$

we shall have

$$\int m\mathbf{WW}\cdot\nabla fd\sigma d\sigma' = \nabla\cdot\{\rho^*\mathbf{VV} + \Lambda^*\}.$$

Also we have

$$\int m\mathbf{W}\frac{\partial f}{\partial t}d\sigma d\sigma' = \frac{\partial}{\partial t}(\rho^*\mathbf{V}),$$

$$\int m\mathbf{g}\cdot\nabla_\xi fd\sigma d\sigma' = 0,$$

$$\int m\mathbf{Wg}\cdot\nabla_\xi fd\sigma d\sigma' = -\rho^*\mathbf{g}^*,$$

where

$$\nabla_\xi = i\frac{\partial}{\partial\xi} + j\frac{\partial}{\partial\eta} + k\frac{\partial}{\partial\zeta}.$$

With this notation we have

$$\int m\mathbf{W}Jd\sigma d\sigma' = \frac{\partial(\rho^*\mathbf{V})}{\partial t} + \nabla\cdot(p^*\mathbf{VV} + \Lambda^*) - \rho^*\mathbf{g}^* + \nabla_\phi(\rho^*\mathbf{N}^*)\mathbf{V} = 0.$$

Finally

$$\rho^*\frac{d\mathbf{V}}{dt} + \nabla\cdot\Lambda^* - \rho^*\mathbf{g}^* + \mathbf{V}\nabla_\phi\cdot(\rho^*\mathbf{N}^*) = 0.$$

The conservation of energy may be treated in a similar manner. The energy of translation for the molecule in question is

$$E = \tfrac{1}{2}m(\xi^2 + \eta^2 + \zeta^2),$$

and for the rotational energy we have

$$K = \tfrac{1}{2}(A\omega_1^2 + B\omega_2^2 + C\omega_3^2),$$

so that the conservation of the total energy gives

$$\int (E + K) J d\sigma d\sigma' = 0.$$

Let us adopt the notation

$$\tfrac{1}{2}\int m\mathbf{U}^2 f d\sigma d\sigma' = \rho^* e_t^*,$$

where e_t^* is the thermal energy per unit mass due to the translational velocity,

$$\int K f d\sigma d\sigma' = \rho^* e_r^*$$

where e_r^* is the thermal energy per unit mass due to the angular velocity;

$$e^* = e_t^* + e_r^*;$$

$$\tfrac{1}{2}\int m\mathbf{U}^2\mathbf{U} f d\sigma d\sigma' = \mathbf{h}^*,$$

where $\mathbf{h}^*$ is thermal current density corresponding to the Fourier conduction of heat;

$$\int (\tfrac{1}{2}m\mathbf{U}^2 + K)\Sigma\dot{\varphi} f d\sigma d\sigma' = \mathbf{S}^*,$$

where $\mathbf{S}^*$ is the energy flux carried by the angular velocity;

$$\int f(\omega_1 L + \omega_2 M + \omega_3 N) d\sigma d\sigma' = q^*,$$

where q^* is the work done by the impressed torque. We further have the following reductions:

$$\tfrac{1}{2}\int m\mathbf{W}^2 f d\sigma d\sigma' = \tfrac{1}{2}\rho^*\mathbf{V}^2 + \rho^* e_t^*,$$

$$\tfrac{1}{2}\int m\mathbf{W}^2\mathbf{W} f d\sigma d\sigma' = \mathbf{V}(\tfrac{1}{2}\rho^*\mathbf{V}^2 + \rho^* e_t^*) + \mathbf{V}\cdot\Lambda^* + \mathbf{h}^*.$$

With these auxiliary formulæ we obtain the energy equation

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\rho^*\mathbf{V}^2 + \rho^* e^*) + \nabla\cdot\{(\tfrac{1}{2}\rho^*\mathbf{V}^2 + \rho^* e^*)\mathbf{V} + \mathbf{V}\cdot\Lambda^* + \mathbf{h}^*\}$$
$$+ \nabla_\phi\cdot\{\tfrac{1}{2}\rho^*\mathbf{V}^2\mathbf{N} + \mathbf{S}^*\} - \mathbf{V}\cdot(\rho^*\mathbf{g}^*) - q^* = 0,$$

which reduces to

$$\rho^*\frac{\partial e^*}{\partial t} + \rho^*\mathbf{V}\cdot\nabla e\cdot + \nabla\cdot(\Lambda^*\cdot\mathbf{V}) + \mathbf{V}\cdot(\nabla\cdot\Lambda^*) + \nabla\cdot\mathbf{h}^*$$
$$- q^* + \nabla_\phi\cdot\{\tfrac{1}{2}\rho^*\mathbf{V}^2\mathbf{N}^* + \mathbf{S}^*\} = 0.$$

The conservation of angular momentum gives the equations

$$\int \Sigma l A\omega_1 J d\sigma d\sigma' = 0,$$

$$\int \Sigma l' A\omega_1 J d\sigma d\sigma' = 0,$$

$$\int \Sigma l'' A\omega_1 J d\sigma d\sigma' = 0.$$

Let us work out the first component. We have

$$\int \Sigma lA\omega_1 \frac{\partial f}{\partial t} d\sigma d\sigma' = \frac{\partial(\rho^* M_1^*)}{\partial t},$$

$$\int \Sigma lA\omega_1 \nabla \cdot (f\mathbf{W}) d\sigma d\sigma' = \nabla \cdot (\rho^* \mathbf{V}\mathbf{M}_1^*),$$

$$\int \Sigma lA\omega_1 \nabla_\xi \cdot (fg) d\sigma d\sigma' = 0.$$

If we write

$$\int f\dot{\varphi} \Sigma lA\omega_1 d\sigma d\sigma' = H_1^*,$$

where H_1^* is expressible as a linear combination of three components of the rotational energy, we have

$$\int \Sigma lA\omega_1 \Sigma \frac{\partial(f\dot{\varphi})}{\partial\varphi} d\sigma d\sigma' + \int \Sigma lA\omega_1 \Sigma \frac{\partial(f\omega_1)}{\partial\omega_1} d\sigma d\sigma'$$

$$= \nabla_\phi \cdot H_1 - \int f(lA\omega_1 + mB\omega_2 + nC\omega_3) d\sigma d\sigma'.$$

The integral reduces further on account of the Euler equations and the equations of the change of the direction cosines, to

$$-\int f(lL + mM + nN) d\sigma d\sigma' = -\mathbf{G}_1^*.$$

By symmetry we obtain the second and third components, so that we have

$$\frac{\partial(\rho^* \mathbf{M}^*)}{\partial t} + \nabla \cdot (\rho^* \mathbf{V}\mathbf{M}^*) + \nabla_\phi \cdot (H^*) - \mathbf{G}^* = 0.$$

Thus we have deduced a complete set of a kind of hydrodynamic equations for six dimensions.

We can, however, further integrate out the angles of orientation and obtain the resulting system of equations in three dimensions. Since the frame of reference for the Euler angles is arbitrary, the condition that f is a continuous function of φ, ψ, and θ implies

$$[f]_{\phi=0}^{\phi=2\pi} = 0, \quad [f]_{\psi=0}^{\psi=2\pi} = 0, \quad \left[\frac{f}{\sin\theta}\right]_{\theta=0}^{\theta=\pi} = 0.$$

The space of integration $d\sigma_A$ is now $d\tau' d\sigma d\sigma'$ instead of $d\sigma d\sigma'$, and we have to redefine our notations in the following fashion,

$$\rho = \int mf d\tau' d\sigma d\sigma', \quad \text{etc.}$$

It will be seen that, by carrying out the integrations, we have, for the conservation of number,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0;$$

for the conservation of translational momentum,

$$\frac{\partial(\rho \mathbf{V})}{\partial t} + \nabla \cdot (\rho \mathbf{V}\mathbf{V} + \Lambda) - \rho \mathbf{g} = 0;$$

for the conservation of energy,

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\rho \mathbf{V}^2 + \rho e) + \nabla \cdot \{(\tfrac{1}{2}\rho \mathbf{V}^2 + \rho e)\mathbf{V} + \mathbf{V} \cdot \Lambda + \mathbf{h}\} - q = 0;$$

for the conservation of moment of momentum,

$$\frac{\partial(\rho \mathbf{M})}{\partial t} + \nabla \cdot (\rho \mathbf{V}\mathbf{M}) - \mathbf{G} = 0.$$

We notice at once that these equations are exactly the same as the preceding set provided we assume the angular divergences ∇_ϕ to be zero. We can further simplify the result if we use the Lagrangian time derivatives[1] instead of the Eulerian time derivatives. Thus

$$\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{V} = 0,$$

$$\rho \frac{d\mathbf{V}}{dt} + \nabla \cdot \Lambda - \rho \mathbf{g} = 0,$$

$$\rho \frac{de}{dt} + \nabla \cdot \mathbf{h} + \nabla \cdot (\Lambda \cdot \mathbf{V}) + \mathbf{V} \cdot (\nabla \cdot \Lambda) - q = 0,$$

$$\rho \frac{d\mathbf{M}}{dt} - \mathbf{G} = 0.$$

The first two equations are the same as for the monatomic gas. But the third equation contains the rotational energy as well as the translational, and there is also a contribution of energy due to the work done by the impressed couple. The last equation is the new statement, which suggests that a gas consisting of nonspherical rigid molecules could propagate a kind of gyroscopic disturbance along with compressional waves of the familiar type.

II. Collision Axiom and the Distribution of Velocities.

In the preceding discussion we defined f as the number of molecules per unit cell. This function f will then depend upon thirteen variables

[1] $\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{V} \cdot \nabla.$

including the time, and our problem is to find these relations. This function f we shall call the distribution function, and assume to be a continuous function with respect to all these variables. Let us call $\rho = \int mf d\tau' d\sigma d\sigma'$ the mass density. The molecular density (say ν) may be absorbed in f, so that we can keep the uniformity of notation. At a given time we can classify all molecules according to twelve properties; then the number of molecules in one of the twelve dimensional cells is

$$f d\tau d\tau' d\sigma d\sigma'.$$

We shall now consider the impact of two molecules which behave like rigid bodies. Let O_1 and O_2 be the two centers of gravity, P the point of impact, and R_1PR_2 the line of impact (normal to the common tangent plane at P) (see Fig. 3). Let the position of P with respect to the principal axes through O_1 be $\mathbf{r}_1$, and the same with respect to those through O_2 be $\mathbf{r}_2$. Let a unit vector along the line of impact with respect to O_1 system be $\mathbf{a}_1$, and the same with respect to O_2 system be $\mathbf{a}_2$. Take for the moments of inertia along the principal axes in these two sets A_1, B_1, C_1; A_2, B_2, C_2 using dyadic notation, then

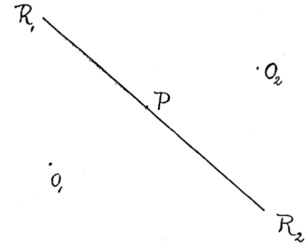

Fig. 3.

$$\Gamma_1 = A_1 i_1 i_1 + B_1 j_1 j_1 + C_1 k_1 k_1,$$

$$\Gamma_2 = A_2 i_2 i_2 + B_2 j_2 j_2 + C_2 k_2 k_2.$$

Take for the mass of the first body m_1, and the second m_2. Let further the translational and the angular velocities of the two bodies before and after impact be

$$\mathbf{W}_1,\ \mathbf{W}_2,\ \mathbf{\Omega}_1,\ \mathbf{\Omega}_2 \quad \text{and} \quad \overline{\mathbf{W}}_1,\ \overline{\mathbf{W}}_2,\ \overline{\mathbf{\Omega}}_1,\ \overline{\mathbf{\Omega}}_2,$$

respectively. If we take R for the measure of the impulse due to the impact, we have the following relations;
for the conservation of translational momentum,

$$m_1\overline{\mathbf{W}_1} = m_1\mathbf{W}_1 + \mathbf{a}_1 R,$$

$$m_2\overline{\mathbf{W}}_2 = m_2\mathbf{W}_2 - \mathbf{a}_2 R;$$

for the conservation of moment of momentum,

$$\Gamma_1 \cdot \overline{\mathbf{\Omega}}_1 = \Gamma_1 \cdot \mathbf{\Omega}_1 + (\mathbf{r}_1 \times \mathbf{a}_1)R,$$

$$\Gamma_2 \cdot \overline{\mathbf{\Omega}}_2 = \Gamma_2 \cdot \mathbf{\Omega}_2 - (\mathbf{r}_2 \times \mathbf{a}_2)R;$$

for the conservation of energy,

$$\frac{m_1}{2}\overline{\mathbf{W}}_1^2+\frac{m_2}{2}\overline{\mathbf{W}}_2^2+\tfrac{1}{2}\overline{\mathbf{\Omega}}_1\cdot\Gamma_1\cdot\overline{\mathbf{\Omega}}_1+\tfrac{1}{2}\overline{\mathbf{\Omega}}_2\cdot\Gamma_2\cdot\overline{\mathbf{\Omega}}_2$$

$$=\frac{m_1}{2}\mathbf{W}_1^2+\frac{m_2}{2}\mathbf{W}_2^2+\tfrac{1}{2}\mathbf{\Omega}_1\cdot\Gamma_1\cdot\mathbf{\Omega}_1+\tfrac{1}{2}\mathbf{\Omega}_2\cdot\Gamma_2\cdot\mathbf{\Omega}_2.$$

From this last equation we can obtain R in terms of the $\mathbf{r}$'s and $\mathbf{a}$'s, substituting the values of the variables before impact for those after impact. Thus

$$R=-2\frac{\mathbf{a}_1\cdot\mathbf{W}_1-\mathbf{a}_2\cdot\mathbf{W}_2+(\mathbf{r}_1\times\mathbf{a}_1)\cdot\mathbf{\Omega}_1-(\mathbf{r}_2\times\mathbf{a}_2)\cdot\mathbf{\Omega}_2}{\frac{1}{m_1}+\frac{1}{m_2}+[(\mathbf{r}\times\mathbf{a}_1)\cdot\Gamma_1^{-1}\cdot(\mathbf{r}_1\times\mathbf{a}_1)]+[(\mathbf{r}_2\times\mathbf{a}_2)\cdot\Gamma_2^{-1}\cdot(\mathbf{r}_2\times\mathbf{a}_2)]}.$$

If moreover the two molecules are of the same kind, $m_1=m_2$ equal to m say, and $\Gamma_1=\Gamma_2=\Gamma$, then

$$R=-2m\frac{\mathbf{a}_1\cdot(\mathbf{W}_1+\mathbf{\Omega}_1\times\mathbf{r}_1)-\mathbf{a}_2\cdot(\mathbf{W}_2+\mathbf{\Omega}_2\times\mathbf{r}_2)}{1+m[(\mathbf{r}_1\times\mathbf{a}_1)\cdot\Gamma\cdot(\mathbf{r}_1\times\mathbf{a}_1)+(\mathbf{r}_2\times\mathbf{a}_2)\cdot\Gamma\cdot(\mathbf{r}_2\times\mathbf{a}_2)]}.$$

If we call the direction of the impulse the normal direction (normal to the surfaces), the normal component of the relative velocity of the point of impact will be given by

$$\mathbf{W}_n=\mathbf{a}_1\cdot(\mathbf{W}_1-\mathbf{r}_1\times\mathbf{\Omega}_1)-\mathbf{a}_2\cdot(\mathbf{W}_2-\mathbf{r}_2\times\mathbf{\Omega}_2).$$

We are now ready to consider the probability of impact of two such molecules. Let us fix our attention only on these two molecules which are going to collide. They will have rotation as well as motion of the center of gravity, and it is necessary for us to observe not only the motion of the centers of gravity but also the behavior of the two points which are going to collide. Let the point of impact of the first body be P and that of the second body be P'. Then if we imagine the first body at rest, P' will describe a curved path before it impinges on P, with such a relative velocity that its normal component may be represented by $\mathbf{W}_n$. Such a path may be found from the differential equations of the motion if we know X, Y, Z and L, M, N.

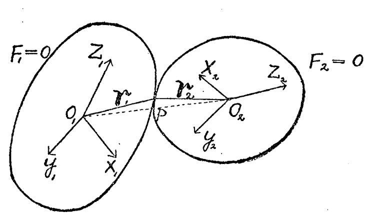

Fig. 4.

As a natural extension of the ordinary supposition in the case of rigid spheres, we shall assume that the probability is proportional to the volume of a cylinder whose base is the element of surface ds at P and whose slant height is the relative velocity of the points of impact.

What we are required to find is, a pair of translational velocities and a pair of angular velocities after impact in terms of those before impact and the parameters which specify the particular type of impact. One formulation is to take two parameters to specify the point of tangency on the first body and to take the remaining three to specify the orientation of the second body with respect to the first body (see Fig 4). Let $F_1(\mathbf{r}_1) = 0$ and $F_2(\mathbf{r}_2) = 0$ be the two surfaces; then the condition of tangency will give

$$\frac{\partial F_1}{\partial x_1} = \lambda\left(\frac{\partial F_2}{\partial x_2} l_2 + \frac{\partial F_2}{\partial y_2} m_2 + \frac{\partial F_2}{\partial x_2} n_2\right),$$

$$\frac{\partial F_1}{\partial y_1} = \lambda\left(\frac{\partial F_2}{\partial x_2} l_2' + \frac{\partial F_2}{\partial y_2} m_2' + \frac{\partial F_2}{\partial z_2} n_2'\right),$$

$$\frac{\partial F_1}{\partial z_1} = \lambda\left(\frac{\partial F_2}{\partial x_2} l_2'' + \frac{\partial F_2}{\partial y_2} m_2'' + \frac{\partial F_2}{\partial z_2} n_2''\right),$$

where

$$\lambda = \pm \frac{\sqrt{\left(\frac{\partial F_1}{\partial x_1}\right)^2 + \left(\frac{\partial F_1}{\partial y_1}\right)^2 + \left(\frac{\partial F_1}{\partial z_1}\right)^2}}{\sqrt{\left(\frac{\partial F_2}{\partial x_2}\right)^2 + \left(\frac{\partial F_2}{\partial y_2}\right)^2 + \left(\frac{\partial F_2}{\partial z_2}\right)^2}}$$

If the normal is taken in the sense of ∇F, the negative sign is taken. Now the set of the direction cosines l_2, m_2, n_2, etc., may be given by three orienting angles say Φ, Ψ, Θ. Then two parameters on the first body, say the longitude and the latitude, will determine $\partial F_1/\partial x_1$, $\partial F/\partial y_1$, $\partial F_1/\partial z_1$, and consequently $\partial F_2/\partial x$, $\partial F_2/\partial y_2$, $\partial F_2/\partial z_2$ and $\mathbf{r}_2$ may be obtained as functions of these five parameters. Let us designate the element of parametric space (with a proper proportionality factor)by dp; then the probability of impact is $|\mathbf{W}_n|dpd\sigma d\sigma'$. Following the usual method[1] let us conceive two classes of molecules say A and B which are both distributed in the element $d\tau d\tau'$ of space at random. We may suppose the translational velocities and moments of momentum to be uniform so that changes occur only at a collision. Let us classify the encounters into two types α and β, where α designates such encounters that before the collision one of the colliding molecules belongs to the class A and the other to the class B, whereas β designates such encounters that after the collision one of the colliding molecules belongs to the class A and the other to the class B, both types having the same line of impact (the common normal) and the same orientations. The number of collisions of α type in unit time per unit cell of τ and τ' space will be

$$ff'|\mathbf{W}_n|dpd\sigma_1 d\sigma_2 d\sigma_1' d\sigma_2',$$

[1] For instance see Jean's "The Dynamical Theory of Gases," Chap. II.

where $d\sigma_1 d\sigma_1'$ refer to the class A and $d\sigma_2 d\sigma_2'$ to the class B; and f and f' are the distribution functions with arguments having subscripts 1 and 2 respectively. Then the total contribution to the class A due to this α type will be given by integrating the above expression over all possible σ_2 and σ_2', namely

$$d\sigma_1 d\sigma_1' \int\int ff' |\mathbf{W}_n| dp d\sigma_2 d\sigma_2'.$$

The number of collisions of type β in unit time per unit cell of τ and τ' space will be

$$\bar{f}\bar{f}' |\overline{\mathbf{W}}_n| \overline{dp} \overline{d\sigma_1} \overline{d\sigma_2} \overline{d\sigma_1}' \overline{d\sigma_2}',$$

where the dashes above the characters express the corresponding functions for the type β, and the total contribution for the class A due to this β type will be, then,

$$\overline{d\sigma_1} \overline{d\sigma_1}' \int\int \bar{f}\bar{f}' |\overline{\mathbf{W}}_n| \overline{dp} \overline{d\sigma_2} \overline{d\sigma_2}'.$$

In this theory we assume central symmetry so that $dp = \overline{dp}$. Therefore the number of molecules in the class A is increased by the difference of the two integral expressions above. The difference may be written in the form

$$d\sigma_1 d\sigma_1' \int\int (\bar{f}\bar{f}' - ff') |\mathbf{W}_n| dp d\sigma_2 d\sigma_2'.$$

This involves the fact that the Jacobian[1] of the transformation is equal to unity and $|\overline{\mathbf{W}}_n| = |\mathbf{W}_n|$.[2]

This is the expression for J from this point of view. Thus we formulate the Boltzmann equation as follows:

$$\frac{df}{dt} d\sigma_1 d\sigma_1' = d\sigma_1 d\sigma_1' \left\{ \frac{\partial f}{\partial t} + \Sigma \frac{\partial (f\dot{x})}{\partial x} + \Sigma \frac{\partial (f\dot{\xi})}{\partial \xi} + \Sigma \frac{\partial (f\dot{\varphi})}{\partial \varphi} + \Sigma \frac{\partial (f\dot{\omega}_1)}{\partial \omega} \right\}$$

$$= d\sigma_1 d\sigma_1' \int (\bar{f}\bar{f}' - ff') |W_n| d\sigma_2 d\sigma_2' dp.$$

Let us define

$$S = -k\int f \log f \, d\sigma_1 d\sigma_1',$$

where $S = -kH$, H being Boltzmann's probability function. We obtain in the familiar way

$$\frac{dS}{dt} = \frac{1}{4} k \int (\log \bar{f}\bar{f}' - \log ff')(\bar{f}\bar{f}' - ff') |W_n| d\sigma_1 d\sigma_2 d\sigma_1' d\sigma_2' dp,$$

showing that dS/dt is always positive or zero, and S is an increasing function or else constant. For the steady state S is a maximum and therefore $dS/dt = 0$, so that we have $\bar{f}\bar{f}' - ff' = 0$. This functional

[1] It may be computed easily from the equation of the transformation to be -1, but since we are concerned only with the numerical value the positive sign is taken.

[2] See Maxwell, Collected Works, Vol. I., p. 407.

equation is equivalent to

$$\log \bar{f} + \log \bar{f}' = \log f + \log f',$$

which is the form of an invariant of the encounters. Therefore

$$\log f = \text{an invariant},$$

is a solution, and the complete solution is a linear combination of all invariants. Thus

$$\log f = \alpha_1 N + \alpha_2(m\mathbf{V}^2 + \boldsymbol{\Omega} \cdot \Gamma \cdot \boldsymbol{\Omega}) + \mathbf{b} \cdot \mathbf{V} + \mathbf{c} \cdot \Gamma \cdot \boldsymbol{\Omega},$$

where α_1, α_2; **b** and **c** are arbitrary constants. Taking the logarithm and rearranging the expression, we have for the distribution function

$$f = \mathcal{C}e^{-\frac{1}{\alpha^2}\left[(\mathbf{V} - \mathbf{V}_0)^2 + \frac{\boldsymbol{\Omega} \cdot \Gamma}{m} \cdot (\boldsymbol{\Omega} - \boldsymbol{\Omega}_0)\right]},$$

and the constants[1] $\mathcal{C}$, α, $\mathbf{V}_0$, $\boldsymbol{\Omega}_0$ are to be determined by the total number, the temperature and the visible motions of translation and rotation.

External Pressure for State of Equilibrium.

We have already found an expression for the impulse, when two rigid bodies impinge on each other. In case of the external pressure, we can simplify the expression, for we can take the plane of the wall as the x-y plane and the axis of z as the direction of the impulse. Thus

$$R = -2m\frac{\mathbf{a} \cdot (\mathbf{W} + \boldsymbol{\Omega} \times \mathbf{r})}{1 + m(\mathbf{r} \times \mathbf{a}) \cdot \Gamma \cdot (\mathbf{r} \times \mathbf{a})},$$

where a has now for its three components l'', m'', n''. It must be noticed that all the vectors in the above expression are referred to the principal axes of the body. The distribution of the orientation being the same as the distribution of the point of tangency o of the x-y plane, we may take the probability of impact to be the product of the normal component of the velocity of the point of contact and the probability of distribution of the z-axis with respect to the center of gravity (see Fig. 5). This latter is given by $1/4\pi \sin \theta \, d\theta d\mu$, where μ is the longitude and θ is the latitude of z on the unit sphere referred to the principal axes. From the geometry of figure we can identify this θ with the previous θ and μ with $\psi + \pi/2$.

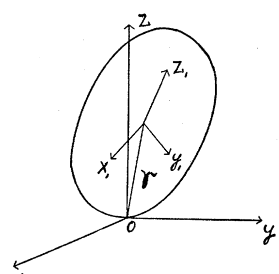

Fig. 5.

[1] These constants may involve x, y, z; ψ, φ, θ; t.

Therefore the probability of impact is

$$|\mathbf{W}_n|\frac{1}{4\pi}\sin\theta d\theta d\psi.$$

Taking the half of this probability because of the assumed central symmetry, we get for the pressure on the x-y plane

$$\frac{1}{8\pi}\int_\sigma\int_{\sigma'}\int_0^{2\pi}\int_0^\pi fR|\mathbf{W}_n|d\sigma d\sigma' \sin\theta d\theta d\psi.$$

where

$$\mathbf{W}_n = l''(\xi+\omega_2 Z_1-\omega_3 y_1)i + m''(\eta+\omega_3 x_1-\omega_1 z_1)j + n''(\zeta+\omega_1 y_1-\omega_2 x_1)k,$$

and

$$R = -2m\frac{l''(\xi+\omega_2 z_1-\omega_3 y_1)+m''(\eta+\omega_3 x_1-w_1 z_1)+n''(\zeta+\omega_1 y_1-\omega_2 x_1)}{1+m\left[\frac{(y_1 n''-z_1 m'')^2}{A}+\frac{(z_1 l''-x_1 n'')^2}{B}+\frac{(x_1 m''-y_1 l'')^2}{C}\right]}$$

in coördinate expression. Since

$$l''=\sin\psi\sin\theta,\quad m''=\cos\psi\sin\theta,\quad n''=\cos\theta,$$

we have

$$\frac{\partial F}{\partial x_1}=\lambda\sin\psi\sin\theta,\quad \frac{\partial F}{\partial y_1}=\lambda\cos\psi\sin\theta,\quad \frac{\partial F}{\partial z_2}=\lambda\cos\theta,$$

and consequently if we know F, we can solve for x, y, z as functions of ψ and θ. We found above the distribution function f, and since the σ and σ' spaces are independent of the form of F and the orienting angles, we can at once effect the $d\sigma$ and $d\sigma'$ integrations.

If we assume the mass motion and the visible rotation zero, the expression for f may be written

$$f = N\mathcal{C}e^{-(1/a^2)[\xi^2+\eta^2+\zeta^2+(1/m)(A\omega_1^2+B\omega_2^2+C\omega_3^2)]},$$

where $\mathcal{C}$ may be determined by integrating this expression over the whole space, namely

$$N = M\mathcal{C}\int\int\int_{-\infty}^{+\infty}\int\int\int e^{-(1/a^2)\{\xi^2+\eta^2\zeta^2+(1/m)(A\omega_1^2+B\omega_{2}^2+C\omega_0^2)\}}d\xi d\eta d\zeta d\omega_1 d\omega_2 d\omega_3$$

giving

$$\mathcal{C} = \frac{1}{\alpha^6\pi^3}\frac{\sqrt{ABC}}{m^{\frac{3}{2}}}.$$

In the expression for the pressure, carrying out the integrations with respect to $d\sigma d\sigma'$

$$p = \frac{mN}{8\pi}\int_0^{2\pi}\int_0^\pi \alpha^2\sin\theta\, d\theta d\psi,$$

and if α is independent of the angle

$$p = Nm\frac{\alpha^2}{2}.$$

Putting

$$\frac{\alpha^2}{2} = kT,$$

$$p = NmkT,$$

giving Boyle-Charles's law for this kind of gas.

The writer wishes to express his gratitude to Professor A. C. Lunn, who has given suggestions in carrying out this work.

Ryerson Physical Laboratory,
University of Chicago,
February 2, 1917.