

VII. *On Stresses in Rarified Gases arising from Inequalities of Temperature.*

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Received March 19,—Read April 11, 1878.

1. IN this paper I have followed the method given in my paper “On the Dynamical Theory of Gases” (Phil. Trans., 1867, p. 49). I have shown that when inequalities of temperature exist in a gas, the pressure at a given point is not the same in all directions, and that the difference between the maximum and the minimum pressure at a point may be of considerable magnitude when the density of the gas is small enough, and when the inequalities of temperature are produced by small* solid bodies at a higher or lower temperature than the vessel containing the gas.

2. The nature of this stress may be thus defined:—Let the distance from a given point, measured in a given direction, be denoted by h ; then the space-variation of the temperature for a point moving along this line will be denoted by $\frac{d\theta}{dh}$, and the space-variation of this quantity along the same line by $\frac{d^2\theta}{dh^2}$.

There will, in general, be a particular direction of the line h for which $\frac{d^2\theta}{dh^2}$ is a maximum, another for which it is a minimum, and a third for which it is a maximum-minimum. These three directions are at right angles to each other, and are the

* The dimensions of the bodies must be of the same order of magnitude as a certain length λ , which may be defined as the distance travelled by a molecule with its mean velocity during the time of relaxation of the medium.

The time of relaxation is the time in which inequalities of stress would disappear if the rate at which they diminish were to continue constant. Hence

$$\lambda = 2 \left(\frac{2p}{\pi\rho} \right)^{\frac{1}{2}} \cdot \frac{\mu}{p} = 2\mu \left(\frac{2}{\pi\rho p} \right)^{\frac{1}{2}}.$$

On the hypothesis that the encounters between the molecules resemble those between “rigid elastic” spheres, the free path of a molecule between two successive encounters has a definite meaning, and if l is its mean value,

$$l = \frac{3}{2} \mu \left(\frac{\pi}{2p\rho} \right)^{\frac{1}{2}} = \frac{3\pi}{8} \lambda = 1.178\lambda.$$

So that the mean path of a molecule may be taken as representing what we mean by “small.”

If the force between the molecules is supposed to be a continuous function of the distance, the free path of a molecule has no longer a definite meaning, and we must fall back on the quantity λ , as defined above.

axes of principal stress at the given point; and the part of the stress arising from inequalities of temperature is, in each of these principal axes,

$$3 \frac{\mu^2}{\rho \theta} \frac{d^2 \theta}{dh^2},$$

where μ is the coefficient of viscosity, ρ the density, and θ the absolute temperature.

3. Now for dry air at 15° C, $\mu = 1.9 \times 10^{-4}$ in centimetre-gramme-second measure, and $\frac{3\mu^2}{\rho\theta} = \frac{1}{p} 0.315$, where p is the pressure, the unit of pressure being one dyne per square centimetre, or nearly one millionth part of an atmosphere.

If a sphere of $2a$ centimetres in diameter is T degrees centigrade hotter than the air at large distances from it, then, when there is a steady flow of heat, the temperature at a distance of r centimetres from the centre will be

$$\theta = \theta_0 + \frac{Ta}{r}, \text{ and } \frac{d^2 \theta}{dr^2} = \frac{2Ta}{r^3}.$$

Hence, at a distance of r centimetres from the centre of the sphere, the pressure in the direction of the radius arising from inequality of temperature will be $\frac{Ta}{pr^3} 0.63$ dynes per square centimetre.

4. In Mr. CROOKES' experiments the pressure, p , was often so small that this stress would be capable, if it existed alone, of producing rapid motion in a radiometer.

Indeed, if we were to consider only the normal part of the stress exerted on solid bodies immersed in the gas, most of the phenomena observed by Mr. CROOKES could be readily explained.

5. Let us take the case of two small bodies symmetrical with respect to the axis joining their centres of figure. If both bodies are warmer than the air at a distance from them, then, in any section perpendicular to the axis joining their centres, the point where it cuts this line will have the highest temperature, and there will be a flow of heat outwards from this axis in all directions.

Hence $\frac{d^2 \theta}{dh^2}$ will be positive for the axis, and it will be a line of maximum pressure, so that the bodies will repel each other.

If both bodies are colder than the air at a distance, everything will be reversed; the axis will be a line of minimum pressure, and the bodies will attract each other.

If one body is hotter and the other colder than the air at a distance, the effect will be smaller, and it will depend on the relative sizes of the bodies, and on their exact temperatures, whether the action is attractive or repulsive.

6. If the bodies are two parallel disks very near to each other, the central parts will produce very little effect, because between the disks the temperature varies uniformly, and $\frac{d^2 \theta}{dh^2} = 0$. Only near the edges will there be any stress arising from inequality of temperature in the gas.

7. If the bodies are encircled by a ring having its axis in the line joining the bodies, then the repulsion between the two bodies, when they are warmer than the air in general, may be converted into attraction by heating the ring so as to produce a flow of heat inwards towards the axis.

8. If a body in the form of a cup or bowl is warmer than the air, the distribution of temperature in the surrounding gas is similar to the distribution of electric potential near a body of the same form, which has been investigated by Sir W. THOMSON. Near the convex surface the value of $\frac{d^2\theta}{dh^2}$ is nearly the same as if the body had been a complete sphere, namely $2T\frac{1}{a^2}$, where T is the excess of temperature, and a is the radius of the sphere. Near the concave surface the variation of temperature is exceedingly small.

Hence the normal pressure will be greater on the convex surface than on the concave surface, and if we were to neglect the tangential pressures we might think this an explanation of the motion of Mr. CROOKES' cups.

Since the expressions for the stress are linear as regards the temperature, everything will be reversed when the cup is colder than the surrounding air.

9. In a spherical vessel, if the two polar regions are made hotter than the equatorial zone, the pressure in the direction of the axis will be greater than that parallel to the equatorial plane, and the reverse will be the case if the polar regions are made colder than the equatorial zone.

10. All such explanations of the observed phenomena must be subjected to careful criticism. They have been obtained by considering the normal stresses alone, to the exclusion of the tangential stresses, and it is much easier to give an elementary exposition of the former than of the latter. If, however, we go on to calculate the forces acting on any portion of the gas in virtue of the stresses on its surface, we find that when the flow of heat is steady, these forces are in equilibrium. Mr. CROOKES tells us that there is no molar current or wind in his radiometer vessels. It is not easy to prove this by experiment, but it is satisfactory to find that the system of stresses here described as arising from inequalities of temperature will not, when the flow of heat is steady, generate currents.

11. Consider, then, the case in which there are no currents of gas but a steady flow of heat, the condition of which is

$$\frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2} = 0.$$

(In the absence of external forces such as gravity, and if the gas in contact with solid bodies does not slide over them, this is always a solution of the equations, and it is the only permanent solution.) In this case the equations of motion show that every particle of the gas is in equilibrium under the stresses acting on it. Hence, any finite portion of the gas is also in equilibrium; also, since the stresses are linear functions of

the temperature, if we superpose one system of temperatures on another, we also superpose the corresponding systems of forces.

Now the system of temperatures due to a solid sphere of uniform temperature immersed in the gas, cannot of itself give rise to any force tending to move the sphere in one direction rather than in another. Let the sphere be placed within the finite portion of gas which, as we have said, is already in equilibrium. The equilibrium will not be disturbed. We may introduce any number of spheres at different temperatures into the portion of gas, so as to form a body of any shape, heated in any manner, and when the flow of heat has become steady the whole system will be in equilibrium.

12. How, then, are we to account for the observed fact that forces act between solid bodies immersed in rarified gases, and this, apparently, as long as inequalities of temperature are maintained?

I think we must look for an explanation in the phenomenon discovered in the case of liquids by HELMHOLTZ and PIOTROWSKI,* and for gases by KUNDT and WARBURG,† that the fluid in contact with the surface of a solid must slide over it with a finite velocity in order to produce a finite tangential stress.

The theoretical treatment of the boundary conditions between a gas and a solid is difficult, and it becomes more difficult if we consider that the gas close to the surface is probably in an unknown state of condensation. We shall therefore accept the results obtained by KUNDT and WARBURG on their experimental evidence.

They have found that the velocity of sliding of the gas over the surface due to a given tangential stress varies inversely as the pressure.

The coefficient of sliding for air on glass was found to be $G = \frac{8}{p}$ centimetres, where p is the pressure in millionths of an atmosphere. Hence at ordinary pressures G is insensible, but in the vessels exhausted by Mr. CROOKES it may be considerable.

Hence, if close to the surface of a solid there is a tangential stress S acting on a surface parallel to that of the body in a direction h parallel to that surface, there will also be a sliding of the gas in contact with the solid over its surface in the direction h with a finite velocity $= \frac{SG}{\mu}$.

13. I have not attempted to enter on the calculation of the effect of this sliding motion, but it is easy to see that if we begin with the case in which there is no sliding, the instantaneous effect of permission being given to the gas to slide must be to diminish the action of all tangential stresses on the surface, without affecting the normal stresses, and in course of time to set up currents sweeping over the surfaces of solid bodies, thus completely destroying the simplicity of our first solution of the problem.

14. When external forces, such as gravity, act on the gas, and when the thermal phenomena produce differences of density in different parts of the vessel, then the well-

* Wiener Sitzb., xl., 1860, p. 607.

† Pogg. Ann., clv., 1875, p. 337.

known convection currents are set up. These also interfere with the simplicity of the problem and introduce very complicated effects. All that we know is that the rarer the gas and the smaller the vessel the less is the effect of the convection currents, so that in Mr. CROOKES' experiments they play a very small part.

We now proceed to the calculations :—

(1.) *Encounter between two Molecules.*

The motion of the two molecules after an encounter depends on their motion before the encounter, and is capable of being determined by purely dynamical methods. If the encounter of the molecules does not cause rotation or vibration in the individual molecules, then the kinetic energy of the centres of mass of the two molecules must be the same after the encounter as it was before.

This will be true on the average, even if the molecules are complex systems capable of rotation and internal vibration, provided the temperature is constant. If, however, the temperature is rising, the internal energy of the molecules is, on the whole, increasing, and therefore the energy of translation of their centres of mass must be, on an average, diminishing at every encounter. The reverse will be the case if the temperature is falling.

But however important this consideration may be in the theory of specific heat and that of the conduction of heat, it has only a secondary bearing on the question of the stresses in the medium; and as it would introduce great complexity and much guess-work into our calculations, I shall suppose that the gas here considered is one the molecules of which do not take up any sensible amount of energy in the form of internal motion. KUNDT and WARBURG* have shown that this is the case with mercury gas.

Let the masses of the molecules be M_1 and M_2 , and their velocity-components ξ_1, η_1, ζ_1 , and ξ_2, η_2, ζ_2 respectively. Let V be the velocity of M_1 relative to M_2 .

Before the encounter let a straight line be drawn through M_1 parallel to V , and let a perpendicular b be drawn from M_2 to this line. The magnitude and direction of b and V will be constant as long as the motion is undisturbed.

During the encounter the two molecules act on each other. If the force acts in the line joining their centres of mass, the product bV will remain constant, and if the force is a function of the distance, V and therefore b will be of the same magnitude after the encounter as before it, but their directions will be turned in the plane of V and b through an angle 2θ , this angle being a function of b and V , which vanishes for values of b greater than the limit of molecular action. Let the plane through V and b make an angle ϕ with the plane through V parallel to x , then all values of ϕ are equally probable.

If ξ_1' be the value of ξ_1 after the encounter,

* Pogg. Ann., clvii., 1876, p. 353.

$$\xi_1' = \xi_1 + \frac{M_2}{M_1 + M_2} ((\xi_2 - \xi_1) 2 \sin^2 \theta + [(\eta_2 - \eta_1)^2 + (\zeta_2 - \zeta_1)^2]^{\frac{1}{2}} \sin 2\theta \cos \phi) \dots \dots (1)$$

When the two molecules are of the same kind, $\frac{M_2}{M_1 + M_2} = \frac{1}{2}$, and in the present investigation of a single gas we shall assume this to be the case.

If we use the symbol δ to indicate the increment of any quantity due to an encounter, and if we remember that all values of ϕ are equally probable, so that the average value of $\cos \phi$ and of $\cos^3 \phi$ is zero, and that of $\cos^2 \phi$ is $\frac{1}{2}$, we find

$$\delta(\xi_1 + \xi_2) = 0 \dots \dots \dots (2)$$

$$\delta(\xi_1^2 + \xi_2^2) = -[3(\xi_2 - \xi_1)^2 - V^2] \sin^2 \theta \cos^2 \theta \dots \dots \dots (3)$$

$$\delta(\xi_1^3 + \xi_2^3) = -\frac{3}{2}(\xi_1 + \xi_2)[3(\xi_2 - \xi_1)^2 - V^2] \sin^2 \theta \cos^2 \theta \dots \dots \dots (4)$$

From these by transformation of coordinates we find

$$\delta(\xi_1 \eta_1 + \xi_2 \eta_2) = -3(\xi_2 - \xi_1)(\eta_2 - \eta_1) \sin^2 \theta \cos^2 \theta \dots \dots \dots (5)$$

$$\begin{aligned} \delta(\xi_1 \eta_1^2 + \xi_2 \eta_2^2) = & -\frac{1}{2}[9(\xi_1 \eta_1^2 + \xi_2 \eta_2^2) - 3(\xi_1 \eta_2^2 + \xi_2 \eta_1^2) \\ & - (\xi_1 + \xi_2)(6\eta_1 \eta_2 + V^2)] \sin^2 \theta \cos^2 \theta \dots \dots \dots (6) \end{aligned}$$

$$\begin{aligned} \delta(\xi_1 \eta_1 \zeta_1 + \xi_2 \eta_2 \zeta_2) = & -\frac{1}{2}[9(\xi_1 \eta_1 \zeta_1 + \xi_2 \eta_2 \zeta_2) - 3(\xi_1 \eta_1 \zeta_2 + \xi_1 \eta_2 \zeta_1 + \xi_1 \eta_2 \zeta_2 + \xi_2 \eta_1 \zeta_1 \\ & + \xi_2 \eta_1 \zeta_2 + \xi_2 \eta_2 \zeta_1)] \sin^2 \theta \cos^2 \theta \dots \dots \dots (7) \end{aligned}$$

[Application of Spherical Harmonics to the Theory of Gases.]

If we suppose the direction of the velocity of M_1 relative to M_2 to be indicated by the position of a point P on a sphere, which we may call the sphere of reference, then the direction of the relative velocity after the encounter will be indicated by a point P', the angular distance PP' being 2θ , so that the point P' lies in a small circle, every position in which is equally probable.

We have to calculate the effect of an encounter upon certain functions of the six velocity-components of the two molecules. These six quantities may be expressed in terms of the three velocity-components of the centre of mass of the two molecules (say u, v, w), the relative velocity of M_1 with respect to M_2 which we call V, and the two angular coordinates which indicate the direction of V. During the encounter, the quantities u, v, w , and V remain the same, but the angular coordinates are altered from those of P to those of P' on the sphere of reference.

Whatever be the form of the function of $\xi_1, \eta_1, \zeta_1, \xi_2, \eta_2, \zeta_2$, we may consider it expressed in the form of a series of spherical harmonics of the angular coordinates, their coefficients being functions of u, v, w, V , and we have only to determine the effect of the encounter upon the value of the spherical harmonics, for their coefficients are not changed.

Let $Y^{(n)}$ be the value at P of the surface harmonic of order n in the series considered.

After the encounter, the corresponding term becomes what $Y^{(n)}$ becomes at the point P', and since all positions of P' in a circle whose centre is P are equally probable, the mean value of the function after the encounter must depend on the mean value of the spherical harmonic in this circle.

Now the mean value of a spherical harmonic of order n in a circle, the cosine of whose radius is μ , is equal to the value of the harmonic at the pole of the circle multiplied by $P^{(n)}(\mu)$, the zonal harmonic of order n , and amplitude μ .

Hence, after the encounter, $Y^{(n)}$ becomes $Y^{(n)}P^{(n)}(\mu)$, and if F_n is the corresponding part of the function to be considered, and δF_n the increment of F_n arising from the encounter, $\delta F_n = F_n(P^{(n)}(\mu) - 1)$.

This is the mean increment of F_n arising from an encounter in which $\cos 2\theta = \mu$. The rate of increment is to be found from this by multiplying it by the number of encounters of each molecule per second in which μ lies between μ and $\mu + d\mu$, and integrating for all values of μ from -1 to $+1$.

This operation requires, in general, a knowledge of the law of force between the molecules, and also a knowledge of the distribution of velocity among the molecules.

When, as in the present investigation, we suppose both the molecules to be of the same kind, and take both molecules into account in the final summation, the spherical harmonics of odd orders will disappear, so that if we restrict our calculations to functions of not more than three dimensions, the effect of the encounters will depend on harmonics of the second order only, in which case $P^{(2)}(\mu) - 1 = \frac{3}{2}(\mu^2 - 1) = \frac{3}{2} \sin^2 2\theta$. —Note added May, 1879.]

(2.) *Number of Encounters in unit of Time.*

We now abandon the dynamical method and adopt the statistical method. Instead of tracing the path of a single molecule and determining the effects of each encounter on its velocity-components and their combinations, we fix our attention on a particular element of volume, and trace the changes in the average values of such combinations of components for all the molecules which at a given instant happen to be within it. The problem which now presents itself may be stated thus: to determine the distribution of velocities among the molecules of any element of the medium, the current-velocity and the temperature of the medium being given in terms of the coordinates and the time. The only case in which this problem has been actually solved is that in which the medium has attained to its ultimate state, in which the temperature is uniform and there are no currents.

Denoting by

$$dN = f_1(\xi, \eta, \zeta, x, y, z, t) d\xi d\eta d\zeta dx dy dz$$

the number of molecules of the kind M_1 which at a given instant are within the element of volume $dx dy dz$, and whose velocity-components lie between the limits $\xi \pm \frac{1}{2}d\xi, \eta \pm \frac{1}{2}d\eta, \zeta \pm \frac{1}{2}d\zeta$, BOLTZMANN has shown that the function f_1 must satisfy the equation

$$\frac{df_1}{dt} + \xi_1 \frac{df_1}{dx} + \eta_1 \frac{df_1}{dy} + \zeta_1 \frac{df_1}{dz} + X \frac{df_1}{d\xi_1} + Y \frac{df_1}{d\eta} + Z \frac{df_1}{d\zeta} + \iiint d\xi_2 d\eta_2 d\zeta_2 \int b db \int d\phi V(f_1 f_2 - f_1' f_2') = 0 \quad \dots \dots \dots (8)$$

where f_2, f_1', f_2' denote what f becomes when in place of the velocity-components of M_1 before the encounter we put those of M_2 before the encounter, and those of M_1 and M_2 after the encounter, respectively, and the integration is extended to all values of ϕ and b and of ξ_2, η_2, ζ_2 , the velocity-components of the second molecule M_2 .

It is impossible, in general, to perform this integration without a knowledge, not only of the law of force between the molecules, but of the form of the functions f_1, f_2, f_1', f_2' , which have themselves to be found by means of the equation.

It is only for particular cases, therefore, that the equation has hitherto been solved.

If the medium is surrounded by a surface through which no communication of energy can take place, then one solution of the equation is given by the conditions

$$f_1 f_2 - f_1' f_2' = 0,$$

and

$$\xi \frac{df}{dx} + \eta \frac{df}{dy} + \zeta \frac{df}{dz} + X \frac{df}{d\xi} + Y \frac{df}{d\eta} + Z \frac{df}{d\zeta} = 0,$$

which give

$$f_1 = A_1 e^{-h(2\psi_1 + \xi^2 + \eta^2 + \zeta^2)} \dots \dots \dots (9)$$

where ψ_1 is the potential of the force whose components are X_1, Y_1, Z_1 , and A_1 is a constant which may be different for each kind of molecules in the medium, but h is the same for all kinds of molecules.

This is the complete solution of this problem, and is independent of any hypothesis as to the manner in which the molecules act on each other during an encounter. The quantity h which occurs in this expression may be determined by finding the mean value of ξ^2 , which is $\frac{1}{2h}$. Now in the kinetic theory of gases,

$$\rho \xi^2 = p = R\rho\theta \quad \dots \dots \dots (10)$$

where p is the pressure, ρ the density, θ the absolute temperature, and R a constant for a given gas. Hence

$$\frac{1}{2h} = R\theta \quad \dots \dots \dots (11)$$

We shall suppose, however, with BOLTZMANN, that in a medium in which there are inequalities of temperature and of velocity

$$dN = N(1 + F(\xi, \eta, \zeta)) f_0(\xi, \eta, \zeta) d\xi d\eta d\zeta \quad \dots \quad (12)$$

where F is a rational function of ξ, η, ζ , which we shall suppose not to contain terms of more than three dimensions, and f_0 is the same function as in equation (9).

Now consider two groups of molecules, each defined by the velocity-components, and let the two groups be distinguished by the suffixes (1) and (2). We have to estimate the number of encounters of a given kind between these two groups in a unit of volume in the time δt , those encounters only being considered for which the limits of b and ϕ are $b \pm \frac{1}{2} db$ and $\phi \pm \frac{1}{2} d\phi$.

Let us first suppose that both groups consist of mere geometrical points which do not interfere with each other's motion. The group dN_1 is moving through the group dN_2 with the relative velocity V , and we have to find how many molecules of the first group approach a molecule of the second group in a manner which would, if the molecules acted on each other, produce an encounter of the given kind. This will be the case for every molecule of the first group which passes through the area $b db d\phi$ in the time δt . The number of such molecules is $dN_1 V b db d\phi \delta t$ for every molecule of the second group, so that the whole number of pairs which pass each other within the given limits is

$$V b db d\phi dN_1 dN_2 \delta t,$$

and if we take the time δt small enough, this will be the number of encounters of the real molecules in the time δt .

(3.) *Effect of the Encounters.*

We have next to estimate the effect of these encounters on the average values of different functions of the velocity-components. The effect of an individual encounter on these functions for the pair of molecules concerned is given in equations (3), (4), (5), (6), (7), each of which is of the form

$$\delta P = Q \sin^2 \theta \cos^2 \theta \quad \dots \quad (13)$$

where P and Q are functions of the velocity-components of the two molecules, and if we write \bar{P} for the average value of P for the N molecules in unit of volume, then taking the sum of the effects of the encounters—

$$\Sigma \delta P = N \delta \bar{P} \quad \dots \quad (14)$$

We thus find

$$\frac{\delta \bar{P}}{\delta t} = N \iiint \iiint \iiint \iiint Q \sin^2 \theta \cos^2 \theta V b db d\phi f_1 f_2 d\xi_1 d\eta_1 d\zeta_1 d\xi_2 d\eta_2 d\zeta_2 \quad \dots \quad (15)$$

Now, since θ is a function of b and V , the definite integral

$$V \int_0^{2\pi} \int_0^\infty b \sin^2 \theta \cos^2 \theta db d\phi = B \quad \dots \quad (16)$$

will be a function of V only.

If the molecules are “rigid-elastic” spheres of diameter s ,

$$B = \frac{1}{6} \pi s^3 V \dots \dots \dots (17)$$

If they repel each other with a force inversely as the fifth power of the distance, so that at a distance r the force is κr^{-5} , then

$$B = \left(\frac{2\kappa}{M}\right)^{\frac{1}{2}} A_2 \dots \dots \dots (18)$$

where A_2 is the numerical quantity 1.3682. In this case B is independent of V .

The experiments of O. E. MEYER,* KUNDT and WARBURG,† PULUJ,‡ Von OBERMAYER,§ EILHARD WIEDEMANN,|| and HOLMAN,¶ show that the viscosity of air varies according to a lower power of the absolute temperature than the first, probably the 0.77 power. If the viscosity had varied as the first power of the absolute temperature, B would have been independent of V . Though this is not the case, we shall assume, for the sake of being able to effect the integrations, that B is independent of V .

We shall find it convenient to write for B ,

$$B = \frac{p}{3N\mu} \dots \dots \dots (19)$$

where p is the hydrostatic pressure, N the number of molecules in unit of volume, and μ a new coefficient which we shall afterwards find to be the coefficient of viscosity.

Equation (15) may now be written

$$\frac{\delta P}{\delta t} = \frac{p}{3\mu} \iiint \iiint Q f_1 f_2 d\xi_1 d\eta_1 d\zeta_1 d\xi_2 d\eta_2 d\zeta_2 \dots \dots \dots (20)$$

where the integrations are all between the limits $-\infty$ and $+\infty$, and f_1 and f_2 are of the form

$$f = (1 + F(\xi, \eta, \zeta)) h^{\frac{3}{2}} \pi^{-\frac{3}{2}} e^{-h(\xi^2 + \eta^2 + \zeta^2)} \dots \dots \dots (21)$$

$F(\xi, \eta, \zeta)$ being small compared with unity.

We may write F in the form

$$\begin{aligned} F = & (2h)^{\frac{3}{2}} (\alpha\xi + \beta\eta + \gamma\zeta) + 2h(\frac{1}{2}\alpha^2\xi^2 + \frac{1}{2}\beta^2\eta^2 + \frac{1}{2}\gamma^2\zeta^2 + \beta\gamma\eta\zeta + \gamma\alpha\zeta\xi + \alpha\beta\xi\eta) \\ & + (2h)^{\frac{3}{2}} (\frac{1}{6}\alpha^3\xi^3 + \frac{1}{6}\beta^3\eta^3 + \frac{1}{6}\gamma^3\zeta^3 + \frac{1}{2}\alpha^2\beta\xi^2\eta + \frac{1}{2}\alpha^2\gamma\xi^2\zeta + \frac{1}{2}\beta^2\gamma\eta^2\zeta \\ & + \frac{1}{2}\beta^2\alpha\eta^2\zeta + \frac{1}{2}\gamma^2\alpha\zeta^2\xi + \frac{1}{2}\gamma^2\beta\zeta^2\eta + \alpha\beta\gamma\xi\eta\zeta) \dots \dots \dots (22) \end{aligned}$$

where each combination of the symbols $\alpha\beta\gamma$ is to be taken as a single independent symbol, and not as a product of the component symbols.

* Pogg. Ann., 1873, Bd. 148, p. 222.

† Pogg. Ann., 1876, Bd. 159, p. 403.

‡ Wiener Sitz., 1874 and 1876.

§ Wiener Sitz., 1875.

|| Arch. des Sci. Phys. et Nat., 1876, t. 56, p. 273.

¶ American Academy of Arts and Sciences, June 14, 1876. Phil. Mag., s. 5, vol. 3, No. 16, Feb., 1877.

(4.) *Mean Values of Combinations of ξ, η, ζ .*

To find the mean value of any function of ξ, η, ζ for all the molecules in the element, we must multiply this function by f , and integrate with respect to ξ, η , and ζ .

If the non-exponential factor of any term contains an odd power of any of the variables, the corresponding part of the integral will vanish, but if it contains only even powers, each even power, such as $2n$, will introduce a factor

$$R^n \theta^n (2n-1)(2n-3) \dots 3 \cdot 1$$

into the corresponding part of the integral.

First, let the function be 1, then

$$1 = \iiint f d\xi d\eta d\zeta \dots \dots \dots (23)$$

or

$$1 = 1 + \frac{1}{2}(\alpha^2 + \beta^2 + \gamma^2) \dots \dots \dots (24)$$

which gives the condition

$$\alpha^2 + \beta^2 + \gamma^2 = 0 \dots \dots \dots (25)$$

Let us next find the mean value of ξ in the same way, denoting the result by the symbol $\bar{\xi}$,

$$\bar{\xi} = (R\theta)^{\frac{1}{2}} \left[\alpha + \frac{1}{2}(\alpha^3 + \alpha\beta^2 + \alpha\gamma^2) \right] \dots \dots \dots (26)$$

Since in what follows we shall denote the velocity-components of each molecule by $u + \xi, v + \eta, w + \zeta$, where u, v, w are the velocity-components of the centre of mass of all the molecules within the element, it follows that the mean values of ξ, η, ζ are each of them zero. We thus obtain the equations

$$\left. \begin{aligned} \alpha + \frac{1}{2}(\alpha^3 + \alpha\beta^2 + \alpha\gamma^2) &= 0 \\ \beta + \frac{1}{2}(\alpha^2\beta + \beta^3 + \beta\gamma^2) &= 0 \\ \gamma + \frac{1}{2}(\alpha^2\gamma + \beta^2\gamma + \gamma^3) &= 0 \end{aligned} \right\} \dots \dots \dots (27)$$

Remembering these conditions, we find that the mean values of combinations of two, three, and four dimensions are of the forms

$$\left. \begin{aligned} \overline{\xi^2} &= R\theta(1 + \alpha^2) \\ \overline{\xi\eta} &= R\theta\alpha\beta \end{aligned} \right\} \dots \dots \dots (28)$$

$$\left. \begin{aligned} \overline{\xi^3} &= (R\theta)^{\frac{3}{2}}\alpha^3 \\ \overline{\xi\eta^2} &= (R\theta)^{\frac{3}{2}}\alpha\beta^2 \\ \overline{\xi\eta\zeta} &= (R\theta)^{\frac{3}{2}}\alpha\beta\gamma \end{aligned} \right\} \dots \dots \dots (29)$$

$$\left. \begin{aligned} \overline{\xi^4} &= 3R^2\theta^2(1+2\alpha^2) \\ \overline{\xi^3\eta} &= 3R^2\theta^2\alpha\beta \\ \overline{\xi^2\eta^2} &= R^2\theta^2(1+\alpha^2+\beta^2) \\ \overline{\xi^2\eta\xi} &= R^2\theta^2\beta\gamma \end{aligned} \right\} \dots \dots \dots (30)$$

(5.) *Rates of Decay of these Mean Values.*

If any term of Q in equation (20) contains symbols belonging to one group alone of the molecules, the corresponding term of the integral may be found from the above table, but if it contains symbols belonging to both groups we must consider the sextuple integral (20). But we shall not find it necessary to do this for terms of not more than three dimensions, for in these, if both groups of symbols occur, the index of one of them must be odd, and the integral vanishes.

We thus find from equations (3), (4), (5), (6), and (7)

$$\frac{\delta}{\delta t}\alpha^2 = -\frac{p}{\mu}\alpha^2 \dots \dots \dots (31)$$

$$\frac{\delta}{\delta t}\alpha\beta = -\frac{p}{\mu}\alpha\beta \dots \dots \dots (32)$$

$$\frac{\delta}{\delta t}\alpha^3 = \frac{1}{2}\frac{p}{\mu}(-2\alpha^3 + \alpha\beta^2 + \alpha\gamma^2) \dots \dots \dots (33)$$

$$\frac{\delta}{\delta t}\alpha\beta^2 = \frac{1}{6}\frac{p}{\mu}(\alpha^3 - 8\alpha\beta^2 + \alpha\gamma^2) \dots \dots \dots (34)$$

$$\frac{\delta}{\delta t}\alpha\beta\gamma = -\frac{3}{2}\frac{p}{\mu}\alpha\beta\gamma \dots \dots \dots (35)$$

[Any rational homogeneous function of $\xi \eta \zeta$ is either a solid harmonic, or a solid harmonic multiplied by a positive integral power of $(\xi^2 + \eta^2 + \zeta^2)$, or may be expressed as the sum of a number of terms of these forms.

If we express any one of these terms as a function of u, v, w, V and the angular coordinates of V , we can determine the rate of change of each of the spherical harmonics of the angular coordinates.

If we then transform the expression back to its original form as a function of $\xi_1, \eta_1, \zeta_1, \xi_2, \eta_2, \zeta_2$, and if we add the corresponding functions for both molecules, we shall obtain an expression for the rate of change of the original function.

Thus among the terms of two dimensions we have the five conjugate solid harmonics

$$\frac{1}{3}(2\xi^2 - \eta^2 - \zeta^2),$$

$$\xi\eta, \quad \xi\zeta,$$

$$\eta^2 - \zeta^2, \quad \eta\zeta.$$

The rate of increase of each of these arising from the encounters of the molecules is found by multiplying it by $-\frac{p}{\mu}$. We may therefore call $\frac{p}{\mu}$ the “modulus of the time of relaxation” of this class of functions.

The function $\xi^2 + \eta^2 + \zeta^2$ is not changed by the encounters.

Homogeneous functions of three dimensions are either solid harmonics of the third order or solid harmonics of the first order multiplied by $\xi^2 + \eta^2 + \zeta^2$, or combinations of these.

The time modulus for solid harmonics of the third order is $\frac{3}{2} \frac{p}{\mu}$.—Note added May, 1879.]

That of ξ , η , or ζ , multiplied by $\xi^2 + \eta^2 + \zeta^2$ is $\frac{2}{3} \frac{p}{\mu}$.

(6.) *Effect of External Forces.*

The only effect of external forces is expressed by equations of the form

$$\frac{\delta u}{\delta t} = X \quad \dots \dots \dots (36)$$

The average values of ξ , η , ζ and their combinations are not affected by external forces.

(7.) *Variation of Mean Values within an Element of Volume.*

We have employed the symbol δ to denote the variation of any quantity within an element, arising either from encounters between molecules or from the action of external forces.

There is a third way, however, in which a variation may occur, namely, by molecules entering the element or leaving it, carrying their properties with them.

We shall use the symbol δ to denote the actual variation within a specified element.

If \overline{MQ} is the average value of any quantity for each molecule within the element, then the quantity in unit of volume is $\rho\overline{Q}$. We have to trace the variation of $\rho\overline{Q}$.

We begin with an element of volume moving with the velocity-components U , V , W , then by the ordinary investigation of the “equation of continuity”

$$\frac{\delta}{\delta t}[\overline{Q\rho}] + \frac{d}{dx}[\overline{Q(u+\xi-U)}] + \frac{d}{dy}[\overline{Q(v+\eta-V)}] + \frac{d}{dz}[\overline{Q(w+\zeta-W)}] = \rho \frac{d}{\delta t}\overline{Q} \quad \dots \dots (37)$$

If after performing the differentiations we make $U=u$, $V=v$, $W=w$, the equation becomes for an element moving with the velocity (u , v , w)

$$\frac{\delta}{\delta t}(\rho Q) + \rho Q \left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right) + \frac{d}{dx}(\rho Q \xi) + \frac{d}{dy}(\rho Q \eta) + \frac{d}{dz}(\rho Q \zeta) = \rho \frac{\delta}{\delta t} Q . . . \quad (38)$$

(8.) *Equation of Density.*

Let us first make $Q=1$, then, since the mass of a molecule is invariable, the equation becomes

$$\frac{\delta \rho}{\delta t} + \rho \left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right) = 0 \quad (39)$$

which is the ordinary "equation of continuity."

Eliminating by means of this equation the second term of the general equation (38) we obtain the more convenient form—

$$\rho \frac{\delta Q}{\delta t} + \frac{d}{dx}(\rho Q \xi) + \frac{d}{dy}(\rho Q \eta) + \frac{d}{dz}(\rho Q \zeta) = \rho \frac{\delta Q}{\delta t} \quad (40)$$

(9.) *Equations of Motion.*

Putting $Q=u+\xi$, this equation becomes

$$\rho \frac{\delta u}{\delta t} + \frac{d}{dx}(\rho \xi^2) + \frac{d}{dy}(\rho \xi \eta) + \frac{d}{dz}(\rho \xi \zeta) = \rho X \quad (41)$$

where any combination of the symbols ξ, η, ζ is to be taken as the average value of that combination.

Substituting their values as given in (28)

$$\rho \frac{\delta u}{\delta t} + R \frac{d}{dx}(\rho \theta) + R \left[\frac{d}{dx}(\rho \theta \alpha^2) + \frac{d}{dy}(\rho \theta \alpha \beta) + \frac{d}{dz}(\rho \theta \alpha \gamma) \right] = \rho X \quad (42)$$

which is one of the three ordinary equations of motion of a medium in which stresses exist.

(10.) *Terms of Two Dimensions.*

Put $Q=(u+\xi)^2$. Since the resulting equation is true whatever be the values of u, v, w , we may, after differentiation, put each of these quantities equal to zero. We shall thus obtain the same result which we might have obtained by elimination between this and the former equations. We find

$$\rho \frac{\delta}{\delta t} \xi^2 + 2\rho \xi^2 \frac{du}{dx} + 2\rho \xi \eta \frac{du}{dy} + 2\rho \xi \zeta \frac{du}{dz} + \frac{d}{dx}(\rho \xi^3) + \frac{d}{dy}(\rho \xi^2 \eta) + \frac{d}{dz}(\rho \xi^2 \zeta) = \rho \frac{\delta}{\delta t} \xi^2 . . \quad (43)$$

or by substituting the mean values of these quantities from (29)

$$\begin{aligned} & \rho \frac{\delta \theta}{\delta t} + \rho \frac{\delta}{\delta t} (\theta \alpha^2) + 2\rho \theta \frac{du}{dx} + 2\rho \theta \left(\alpha^2 \frac{du}{dx} + \alpha \beta \frac{du}{dy} + \alpha \gamma \frac{du}{dz} \right) \\ & + R^{\frac{1}{2}} \left[\frac{d}{dx} (\rho \theta^3 \alpha^3) + \frac{d}{dy} (\rho \theta^3 \alpha^2 \beta) + \frac{d}{dz} (\rho \theta^3 \alpha^2 \gamma) \right] = - \frac{R \rho^2 \theta^2}{\mu} \alpha^2 \dots \dots \dots (44) \end{aligned}$$

with two other equations of similar form.

Similarly we obtain by putting $Q = (u + \xi)(v + \eta)$

$$\begin{aligned} & \rho \frac{\delta}{\delta t} (\theta \alpha \beta) + \rho \theta \left(\frac{dv}{dx} + \frac{du}{dy} \right) \\ & + \rho \theta \left(\alpha^2 \frac{dv}{dx} + \alpha \beta \frac{dv}{dy} + \alpha \gamma \frac{dv}{dz} + \alpha \beta \frac{du}{dx} + \beta^2 \frac{du}{dy} + \beta \gamma \frac{du}{dz} \right) \\ & + R^{\frac{1}{2}} \left[\frac{d}{dx} (\rho \theta^3 \alpha^2 \beta) + \frac{d}{dy} (\rho \theta^3 \alpha \beta^2) + \frac{d}{dz} (\rho \theta^3 \alpha \beta \gamma) \right] = - \frac{R \rho^2 \theta^2}{\mu} \alpha \beta \dots \dots \dots (45) \end{aligned}$$

with two other equations of like form for $\beta \gamma$ and $\gamma \alpha$.

(11.) *Terms of Three Dimensions.*

Putting $Q = (u + \xi)^3$ and in the final equation making $u = v = w = 0$ and eliminating $\frac{\delta u}{\delta t}$ by (41) we find

$$\begin{aligned} & \rho \frac{\delta}{\delta t} \xi^3 + 3\rho \xi^3 \frac{du}{dx} + 3\rho \xi^2 \eta \frac{du}{dy} + 3\rho \xi^2 \zeta \frac{du}{dz} \\ & + \frac{d}{dx} (\rho \xi^4) + \frac{d}{dy} (\rho \xi^3 \eta) + \frac{d}{dz} (\rho \xi^3 \zeta) \\ & - 3\xi^2 \left[\frac{d}{dx} (\rho \xi^2) + \frac{d}{dy} (\rho \xi \eta) + \frac{d}{dz} (\rho \xi \zeta) \right] = \rho \frac{\delta}{\delta t} \xi^3 \dots \dots \dots (46) \end{aligned}$$

which gives

$$\begin{aligned} & R^{\frac{1}{2}} \rho \frac{\delta}{\delta t} (\theta^3 \alpha^2) + 3\rho (R\theta)^{\frac{1}{2}} \left(\alpha^3 \frac{du}{dx} + \alpha^2 \beta \frac{du}{dy} + \alpha^2 \gamma \frac{du}{dz} \right) \\ & + 3R^2 \rho \theta \frac{d\theta}{dx} + 3R^2 \rho \theta \left(\alpha^2 \frac{d\theta}{dx} + \alpha \beta \frac{d\theta}{dy} + \alpha \gamma \frac{d\theta}{dz} \right) + 3R^2 \rho \theta \frac{d}{dx} (\alpha^2 \theta) \\ & - 3R^2 \theta \alpha^2 \left[\frac{d}{dx} (\rho \theta \alpha^2) + \frac{d}{dy} (\rho \theta \alpha \beta) + \frac{d}{dz} (\rho \theta \alpha \gamma) \right] = \rho (R\theta)^{\frac{1}{2}} \frac{p}{2\mu} (-2\alpha^3 + \alpha\beta^2 + \alpha\gamma^2) \dots \dots \dots (47) \end{aligned}$$

Since the combinations of $\alpha\beta\gamma$ represent small numerical quantities, we may at this stage of the calculation, when we are dealing with terms of the third order, neglect terms involving them, except when they are multiplied by the large coefficient p/μ . The equation may then be written approximately :—

$$3R^2\rho\theta\frac{d\theta}{dx}=\rho(R\theta)^{\frac{1}{2}}\frac{p}{\mu}(-2\alpha^3+\alpha\beta^2+\alpha\gamma^2) \dots \dots \dots (48)$$

Similarly, by putting $Q=(u+\xi)(v+\eta)^2$, we obtain the approximate equation

$$R^2\rho\theta\frac{d\theta}{dx}=\rho(R\theta)^{\frac{1}{6}}\frac{p}{\mu}(\alpha^3-8\alpha\beta^2+\alpha\gamma^2) \dots \dots \dots (49)$$

and in the same way we find

$$R^3\rho\theta\frac{d\theta}{dx}=\rho(R\theta)^{\frac{1}{6}}\frac{p}{\mu}(\alpha^3+\alpha\beta^2-8\alpha\gamma^2) \dots \dots \dots (50)$$

(12.) *Approximate Values of Terms of Three Dimensions.*

From equations (48), (49), and (50), we find

$$\left. \begin{aligned} \alpha^3 &= -\frac{9}{2} \frac{\mu}{p} \left(\frac{R}{\theta}\right)^{\frac{3}{2}} \frac{d\theta}{dx}, & \alpha\beta^2 = \alpha\gamma^2 &= -\frac{3}{2} \frac{\mu}{p} \left(\frac{R}{\theta}\right)^{\frac{3}{2}} \frac{d\theta}{dx} \end{aligned} \right\}$$

From which by substitution we obtain

$$\left. \begin{aligned} \beta^3 &= -\frac{9}{2} \frac{\mu}{p} \left(\frac{R}{\theta}\right)^{\frac{3}{2}} \frac{d\theta}{dy}, & \alpha^2\beta = \beta\gamma^2 &= -\frac{3}{2} \frac{\mu}{p} \left(\frac{R}{\theta}\right)^{\frac{3}{2}} \frac{d\theta}{dy} \\ \gamma^3 &= -\frac{9}{2} \frac{\mu}{p} \left(\frac{R}{\theta}\right)^{\frac{3}{2}} \frac{d\theta}{dz}, & \alpha^2\gamma = \beta^2\gamma &= -\frac{3}{2} \frac{\mu}{p} \left(\frac{R}{\theta}\right)^{\frac{3}{2}} \frac{d\theta}{dz} \end{aligned} \right\} \dots \dots \dots (51)$$

The value of $\alpha\beta\gamma$ is of a smaller order of magnitude, and we do not require it in this investigation.

(13.) *Equation of Temperature.*

Adding the three equations of the form (44), and omitting terms containing small quantities of two dimensions, and also products of differential coefficients such as $\frac{d\mu}{dx} \frac{d\theta}{dx}$, we find

$$\frac{\partial\theta}{\partial t} = \frac{5}{2} \frac{\mu}{\rho} \left(\frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2} \right) + \frac{2}{3} \frac{\theta}{\rho} \frac{\partial\rho}{\partial t} \dots \dots \dots (52)$$

The first term of the second member represents the rate of increase of temperature due to conduction of heat, as in FOURIER'S Theory, and the second term represents the increase of temperature due to increase of density. We must remember that the gas here considered is one for which the ratio of the specific heats is 1.66.

(14.) *Stresses in the Gas.*

Subtracting one-third of the sum of the three equations from (44), we obtain

$$p\alpha^2 = -2\mu \frac{du}{dx} + \frac{2}{3}\mu \left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right) + 3\frac{\mu^2}{\rho\theta} \frac{d^2\theta}{dx^2} + \frac{3}{2}\frac{\mu^2}{\rho\theta} \left(\frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2} \right) \dots \dots (53)$$

This equation gives the excess of the normal pressure in x above the mean hydrostatic pressure p . The first two terms of the second member represent the effect of viscosity in a moving fluid, and are identical with those given by Professor STOKES (Cambridge Transactions, vol. viii., 1845, p. 297). The last two terms represent the part of the stress which arises from inequality of temperature, which is the special subject of this paper.

There are two other equations of similar form for the normal stresses in y and z .

The tangential stress in the plane xy is given by the equation

$$p\alpha\beta = -\mu \left(\frac{du}{dy} + \frac{dv}{dx} \right) + 3\frac{\mu^2}{\rho\theta} \frac{d^2\theta}{dx dy} \dots \dots \dots (54)$$

There are two other equations of similar form for the tangential stresses in the planes of yz and zx .

(15.) *Final Equations of Motion.*

We are now prepared to complete the equations of motion by inserting in (42) the values of the quantities α^2 , $\alpha\beta$, $\alpha\gamma$, and we find for the equation in x

$$\begin{aligned} \rho \frac{\delta u}{\delta t} + \frac{dp}{dx} - \mu \left(\frac{d^2u}{dx^2} + \frac{d^2u}{dy^2} + \frac{d^2u}{dz^2} \right) + \frac{1}{3}\mu \frac{d}{dx} \left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right) \\ + \frac{9}{2} \frac{\mu^2}{\rho\theta} \frac{d}{dx} \left(\frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2} \right) = \rho X \dots \dots \dots (55) \end{aligned}$$

If we write

$$p' = p + \frac{1}{3}\mu \left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right) + \frac{9}{2} \frac{\mu^2}{\rho\theta} \left(\frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2} \right) \dots \dots \dots (56)$$

$$= p + \frac{9}{5} \frac{\mu}{\theta} \frac{\delta\theta}{\delta t} - \frac{23}{15} \frac{\mu}{\rho} \frac{\delta\rho}{\delta t} \dots \dots \dots (57)$$

or, if the pressure p is constant, so that $\rho\delta\theta + \theta\delta\rho = 0$

$$p' = p + \frac{10}{3} \frac{\mu}{\theta} \frac{\delta\theta}{\delta t} \dots \dots \dots (58)$$

then the equation (55) may be written

$$\rho \frac{\delta u}{\delta t} + \frac{dp'}{dx} - \mu \left(\frac{d^2u}{dx^2} + \frac{d^2u}{dy^2} + \frac{d^2u}{dz^2} \right) = \rho X \dots \dots \dots (59)$$

If there are no external forces such as gravity, then one solution of the equations is

$$u=v=w=0, p'=\text{constant},$$

and if the boundary conditions are such that this solution is consistent with them, it will become the actual solution as soon as the initial motions, if any exist, have subsided. This will be the case if no slipping is possible between the gas and solid bodies in contact with it.

But if such slipping is possible, then wherever in the above solution there is a tangential stress in the gas at the surface of a solid or liquid, there cannot be equilibrium, but the gas will begin to slide over the surface till the velocity of sliding has produced a frictional resistance equal and opposite to the tangential stress. When this is the case the motion may become steady. I have not, however, attempted to enter into the calculation of the state of steady motion.

[I have recently applied the method of spherical harmonics, as described in the notes to sections (1) and (5), to carrying the approximations two orders higher. I expected that this would have involved the calculation of two new quantities, namely, the rates of decay of spherical harmonics of the fourth and sixth orders, but I found that, to the order of approximation required, all harmonics of the fourth and sixth orders may be neglected, so that the rate of decay of harmonics of the second order, the time-modulus of which is $\mu \div p$, determines the rate of decay of all functions of less than 6 dimensions.

The equations of motion, as here given (equation 55) contain the second derivatives of u, v, w , with respect to the coordinates, with the coefficient μ . I find that in the more approximate expression there is a term containing the fourth derivatives of u, v, w , with the coefficient $\mu^3 \div \rho p$.

The equations of motion also contain the third derivatives of θ with the coefficient $\mu^2 \div \rho \theta$. Besides these terms, there is another set consisting of the fifth derivatives of θ with the coefficient $\mu^4 \div \rho^2 p \theta$.

It appears from the investigation that the condition of the successful use of this method of approximation is that $l \frac{d}{dh}$ should be small, where $\frac{d}{dh}$ denotes differentiation with respect to a line drawn in any direction. In other words, the properties of the medium must not be sensibly different at points within a distance of each other, comparable with the "mean free path" of a molecule.—Note added June, 1879.]

APPENDIX.

(Added May, 1879.)

In the paper as sent in to the Royal Society, I made no attempt to express the conditions which must be satisfied by a gas in contact with a solid body, for I thought it very unlikely that any equations I could write down would be a satisfactory representation of the actual conditions, especially as it is almost certain that the stratum of gas nearest to a solid body is in a very different condition from the rest of the gas.

One of the referees, however, pointed out that it was desirable to make the attempt, and indicated several hypothetical forms of surfaces which might be tried. I have therefore added the following calculations, which are carried to the same degree of approximation as those for the interior of the gas.

It will be seen that the equations I have arrived at express both the fact that the gas may slide over the surface with a finite velocity, the previous investigations of which have been already mentioned;* and the fact that this velocity and the corresponding tangential stress are affected by inequalities of temperature at the surface of the solid, which give rise to a force tending to make the gas slide along the surface from colder to hotter places.

This phenomenon, to which Professor OSBORNE REYNOLDS has given the name of Thermal Transpiration, was discovered entirely by him. He was the first to point out that a phenomenon of this kind was a necessary consequence of the Kinetic Theory of Gases, and he also subjected certain actual phenomena, of a somewhat different kind, indeed, to measurement, and reduced his measurements by a method admirably adapted to throw light on the relations between gases and solids.

It was not till after I had read Professor REYNOLDS' paper that I began to reconsider the surface conditions of a gas, so that what I have done is simply to extend to the surface phenomena the method which I think most suitable for treating the interior of the gas. I think that this method is, in some respects, better than that adopted by Professor REYNOLDS, while I admit that his method is sufficient to establish the existence of the phenomena, though not to afford an estimate of their amount.

The method which I have adopted throughout is a purely statistical one. It considers the mean values of certain functions of the velocities within a given element of the medium, but it never attempts to trace the motion of a molecule, not even so far as to estimate the length of its mean path. Hence all the equations are expressed in the forms of the differential calculus, in which the phenomena at a given place are connected with the space variations of certain quantities at that place, but in which no quantity appears which explicitly involves the condition of things at a finite distance from that place.

The particular functions of the velocities which are here considered are those of one, two, and three dimensions. These are sufficient to determine approximately the prin-

* Sect. 12 of introduction.

cipal phenomena in a gas which is not very highly rarified, and in which the space-variations within distances comparable to λ are not very great.

The same method, however, can be extended to functions of higher degrees, and by a sufficient number of such functions any distribution of velocities, however abnormal, may be expressed. The labour of such an approximation is considerably diminished by the use of the method of spherical harmonics as indicated in the note to Section I. of the paper.

On the Conditions to be Satisfied by a Gas at the Surface of a Solid Body.

As a first hypothesis, let us suppose the surface of the body to be a perfectly elastic smooth fixed surface, having the apparent shape of the solid, without any minute asperities.

In this case, every molecule which strikes the surface will have the normal component of its velocity reversed, while the other components will not be altered by impact.

The rebounding molecules will therefore move as if they had come from an imaginary portion of gas occupying the space really filled by the solid, and such that the motion of every molecule close to the surface is the optical reflection in that surface of the motion of a molecule of the real gas.

In this case we may speak of the rebounding molecules close to the surface as constituting the *reflected* gas. All directed properties of the incident gas are reflected, or, as Professor LISTING might say, *perverted* in the reflected gas; that is to say, the properties of the incident and the reflected gas are symmetrical with respect to the tangent plane of the surface.

The incident and reflected gas together constitute the actual gas close to the surface. The actual gas, therefore, cannot exert any stress on the surface, except in the direction of the normal, for the oblique components of stress in the incident and reflected gas will destroy one another.

Since gases can actually exert oblique stress against real surfaces, such surfaces cannot be represented as perfectly reflecting surfaces.

If a molecule, whose velocity is given in direction and magnitude, but whose line of motion is not given in position, strikes a fixed elastic sphere, its velocity after rebound may with equal probability be in any direction.

Consider, therefore, a stratum in which fixed elastic spheres are placed so far apart from one another that any one sphere is not to any sensible extent protected by any other sphere from the impact of molecules, and let the stratum be so deep that no molecule can pass through it without striking one or more of the spheres, and let this stratum of fixed spheres be spread over the surface of the solid we have been considering, then every molecule which comes from the gas towards the surface must strike one or more of the spheres, after which all directions of its velocity become equally probable.

When, at last, it leaves the stratum of spheres and returns into the gas, its velocity

must of course be *from* the surface, but the probability of any particular magnitude and direction of the velocity will be the same as in a gas at rest with respect to the surface.

The distribution of velocity among the molecules which are leaving the surface will therefore be the same as if, instead of the solid, there were a portion of gas at rest, having the temperature of the solid, and a density such that the number of molecules which pass from it through the surface in a given time is equal to the number of molecules of the real gas outside which strike the surface.

To distinguish the molecules, which, after being entangled in the stratum of spheres, afterwards return into the surrounding gas, we shall call them, collectively, the *absorbed and evaporated* gas.

If the spheres are so near together that a considerable part of the surface of each sphere of the outer layer is shielded from the direct impact of the incident molecules by the spheres which lie next to it, then if we call that point of each sphere which lies furthest from the solid the *pole* of the sphere, a greater proportion of molecules will strike any one of the outer layer of spheres near its pole than near its equator, and the greater the obliquity of incidence of the molecule, the greater will be the probability that it will strike a sphere near its pole.

The direction of the rebounding molecule will no longer be with equal probability in all directions, but there will be a greater probability of the tangential part of its velocity being in the direction of the motion before impact, and of its normal part being opposite to the normal part before impact.

The condition of the molecules which leave the surface will therefore be intermediate between that of evaporated gas and that of reflected gas, approaching most nearly to evaporated gas at normal incidence and most nearly to reflected gas at grazing incidence.

If the spheres, instead of being hard elastic bodies, are supposed to act on the molecules at finite, though small distances, and if they are so close together that their spheres of action intersect, then the gas which leaves the surface will be still more like reflected gas, and less like evaporated gas.

We might also consider a surface on which there are a great number of minute asperities of any given form, but since in this case there is considerable difficulty in calculating the effect when the direction of rebound from the first impact is such as to lead to a second or third impact, I have preferred to treat the surface as something intermediate between a perfectly reflecting and a perfectly absorbing surface, and, in particular, to suppose that of every unit of area a portion f absorbs all the incident molecules, and afterwards allows them to evaporate with velocities corresponding to those in still gas at the temperature of the solid, while a portion $1-f$ perfectly reflects all the molecules incident upon it.

We shall begin by supposing that the surface is the plane yz , and that the gas is on that side of it for which x is positive.

The incident molecules are those which, close to the surface, have their normal component of velocity negative. We shall distinguish these molecules by the suffix (1). For these, and these only, ξ_1 is negative.

The rebounding molecules are those which have ξ positive. We shall distinguish them by the suffix (2). Those which are evaporated will be further distinguished by an accent.

Symbols without any mark refer to the whole gas, incident, reflected, and evaporated, close to the surface.

The quantity of gas which is incident on unit of surface in unit of time, is $-\rho_1\xi_1$.

Of this quantity the fraction $1-f$ is reflected, so that the sign of ξ is reversed, and the fraction f is evaporated, the mean value of ξ in evaporated gas being ξ' , where the accent distinguishes symbols belonging to unpolarized gas at rest relative to the surface, and having the temperature, θ' , of the solid.

Equating the quantity of gas which is incident on the absorbing part of the surface to that which is evaporated from it, we have

$$f\rho_1\xi_1+f\rho_2'\xi_2'=0 \quad \dots \dots \dots (60)$$

Equating the whole quantity of gas which leaves the surface to the reflected and evaporated portions

$$\rho_2\xi_2=(f-1)\rho_1\xi_1+f\rho_2'\xi_2' \quad \dots \dots \dots (61)$$

If we next consider the momentum of the molecules in the direction of y , that of the incident molecules is $\rho_1\xi_1\eta_1$. A fraction $(1-f)$ of this is reflected and becomes $(1-f)\rho_1\xi_1\eta_1$, and a fraction f of it is absorbed and then evaporated, the mean value of η being now $-v$, namely, the velocity of the surface relatively to the gas in contact with it.

The momentum of the evaporated portion in the direction of y is therefore $-f\rho_2'\xi_2'v$, and this, together with the reflected portion, makes up the whole momentum which is leaving the surface, or

$$\rho_2\xi_2\eta_2=(f-1)\rho_1\xi_1\eta_1-f\rho_2'\xi_2'v \quad \dots \dots \dots (62)$$

Eliminating $f\rho_2'\xi_2'$ between equations (61) and (62)

$$(1-f)\rho_1\xi_1\eta_1+\rho_2\xi_2\eta_2+v[(1-f)\rho_1\xi_1+\rho_2\xi_2]=0 \quad \dots \dots \dots (63)$$

The values of functions of ξ , η and ζ for the incident molecules are to be found by multiplying the expression in equation (22) by the given function, and integrating with respect to ξ between the limits $-\infty$ and 0, and with respect to η and ζ between the limits $\pm\infty$.

The values of the same functions for the molecules which are leaving the surface are to be found by integrating with respect to ξ from 0 to ∞ .

We must remember, however, that since there is an essential discontinuity in the

conditions of the gas at the surface, the expression in equation (22) is a much less accurate approximation to the actual distribution of velocities in the gas close to the surface than it is in the interior of the gas. We must, therefore, consider the surface conditions at which we arrive in this way as liable to important corrections when we shall have discovered more powerful methods of attacking the problem.

For the present, however, we consider only terms of three dimensions or less, and we find

$$\left. \begin{aligned} \rho_1 \xi_1 &= -\rho(2\pi)^{-\frac{1}{2}}(R\theta)^{\frac{1}{2}}(1 + \frac{1}{2}\alpha^2) \\ \rho_2 \xi_2 &= \rho(2\pi)^{-\frac{1}{2}}(R\theta)^{\frac{1}{2}}(1 + \frac{1}{2}\alpha^2) \end{aligned} \right\} \dots \dots \dots (64)$$

$$\left. \begin{aligned} \rho_1 \xi_1 \eta_1 &= \frac{1}{2}\rho R\theta\alpha\beta - \frac{1}{2}\rho(2\pi)^{-\frac{1}{2}}R\theta\alpha^2\beta \\ \rho_2 \xi_2 \eta_2 &= \frac{1}{2}\rho R\theta\alpha\beta + \frac{1}{2}\rho(2\pi)^{-\frac{1}{2}}R\theta\alpha^2\beta \end{aligned} \right\} \dots \dots \dots (65)$$

Substituting these expressions in equation (63), and neglecting α^2 in comparison with unity, we find

$$(2-f)\rho R\theta\alpha\beta + f(2\pi)^{-\frac{1}{2}}\rho R\theta\alpha^2\beta + 2f(2\pi)^{-\frac{1}{2}}(1 + \frac{1}{2}\alpha^2)(R\theta)^{\frac{1}{2}}\rho v = 0 \dots \dots (66)$$

If we write

$$G = \frac{1}{2}\mu(2\pi)^{\frac{1}{2}}(p\rho)^{-\frac{1}{2}}\left(\frac{2}{f}-1\right) \dots \dots \dots (67)$$

and substitute for $\alpha\beta$ and $\alpha^2\beta$ their values as given in equations (54) and (51), and divide by $2(p\rho)^{\frac{1}{2}}$, equation (66) becomes

$$v - G\left(\frac{dv}{dx} - \frac{3}{2}\frac{\mu}{\rho\theta}\frac{d^2\theta}{dx^2}\right) - \frac{3}{4}\frac{\mu}{\rho\theta}\frac{d\theta}{dy} = 0 \dots \dots \dots (68)$$

If there is no inequality of temperature, this equation is reduced to

$$v = G\frac{dv}{dx} \dots \dots \dots (69)$$

If, therefore, the gas at a finite distance from the surface is moving parallel to the surface, the gas in contact with the surface will be sliding over it with the finite velocity v , and the motion of the gas will be very nearly the same as if the stratum of depth G had been removed from the solid and filled with the gas, there being now no slipping between the new surface of the solid and the gas in contact with it.

The coefficient G was introduced by HELMHOLTZ and PIOTROWSKI under the name of *Gleitungs-coefficient*, or coefficient of slipping. The dimensions of G are those of a line, and its ratio to l , the mean free path of a molecule, is given by the equation

$$G = \frac{2}{3}\left(\frac{2}{f}-1\right)l \dots \dots \dots (70)$$

KUNDT and WARBURG found that for air in contact with glass, $G=2l$, whence we find $f=\frac{1}{2}$, or the surface acts as if it were half perfectly reflecting and half perfectly absorbent. If it were wholly absorbent, $G=\frac{2}{3}l$.

It is easy to write down the surface conditions for a surface of any form. Let the direction-cosines of the normal ν be l, m, n , and let us write

$$\frac{d}{d\nu} \text{ for } l \frac{d}{dx} + m \frac{d}{dy} + n \frac{d}{dz}.$$

We then find as the surface conditions

$$\left. \begin{aligned} u - G \frac{d}{d\nu} [(1-l^2)u - lmv - lnw] + \frac{3}{4} \frac{\mu}{\rho\theta} \left(\frac{d}{dx} - l \frac{d}{d\nu} \right) \left(\theta + 4G \frac{d\theta}{d\nu} \right) &= 0 \\ v - G \frac{d}{d\nu} [(1-m^2)v - mnw - mln] + \frac{3}{4} \frac{\mu}{\rho\theta} \left(\frac{d}{dy} - m \frac{d}{d\nu} \right) \left(\theta + 4G \frac{d\theta}{d\nu} \right) &= 0 \\ w - G \frac{d}{d\nu} [(1-n^2)w - nlu - nmv] + \frac{3}{4} \frac{\mu}{\rho\theta} \left(\frac{d}{dz} - n \frac{d}{d\nu} \right) \left(\theta + 4G \frac{d\theta}{d\nu} \right) &= 0 \end{aligned} \right\} \quad (71)$$

In each of these equations the first term is one of the velocity-components of the gas in contact with the surface, which is supposed fixed; the second term depends on the slipping of the gas over the surface, and the third term indicates the effect of inequalities of temperature of the gas close to the surface, and shows that in general there will be a force urging the gas from colder to hotter parts of the surface.

Let us take as an illustration the case of a capillary tube of circular section, and for the sake of easy calculation we shall suppose that the motion is so slow, and the temperature varies so gradually along the tube that we may suppose the temperature uniform throughout any one section of the tube.

Taking the axis of the tube for that of z , we have for the condition of steady motion parallel to the axis

$$\frac{dp}{dz} - \mu \left(\frac{d^2w}{dx^2} + \frac{d^2w}{dy^2} \right) \dots \dots \dots (72)$$

Since everything is symmetrical about the axis, if we write r^2 for $x^2 + y^2$ we find as the solution of this equation

$$w = A + \frac{1}{4\mu} \frac{dp}{dz} r^2 \dots \dots \dots (73)$$

If Q denotes the quantity of gas which passes through a section of the tube in unit of time

$$\begin{aligned} Q &= 2\pi \int \rho w r dr \\ &= \pi \rho a^2 \left(A + \frac{1}{8\mu} \frac{dp}{dz} a^2 \right) \dots \dots \dots (74) \end{aligned}$$

At the inner surface of the tube we have $r = a$, and

$$\begin{aligned} w &= A + \frac{1}{4\mu} \frac{dp}{dz} a^2 \\ &= \frac{Q}{\pi \rho a^2} + \frac{1}{8\mu} \frac{dp}{dz} a^2 \dots \dots \dots (75) \end{aligned}$$

also

$$\frac{dw}{dv} = -\frac{1}{2\mu} \frac{dp}{dz} \alpha \quad \dots \dots \dots (76)$$

The last of equations (71) may therefore be written

$$\frac{Q}{\pi \rho a^2} + \frac{1}{8\mu} (\alpha^2 + 4G\alpha) \frac{dp}{dz} - \frac{3}{4} \frac{\mu}{\rho \theta} \frac{d\theta}{dz} = 0 \quad \dots \dots \dots (77)$$

Equation (77) gives the relation between the quantity of gas which passes through any section of the tube, the rate of variation of pressure, and the rate of variation of temperature in passing along the axis of the tube.

If the pressure is uniform there will be a flow of gas from the colder to the hotter end of the tube, and if there is no flow of gas the pressure will increase from the colder to the hotter end of the tube.

These effects of the variation of temperature in a tube have been pointed out by Professor OSBORNE REYNOLDS as a result of the Kinetic Theory of Gases, and have received from him the name of Thermal Transpiration: a name in strict analogy with the use of the word Transpiration by GRAHAM.

But the phenomenon actually observed by Professor REYNOLDS in his experiments was the passage of gas through a porous plate, not through a capillary tube; and the passage of gases through porous plates, as was shown by GRAHAM, is of an entirely different kind from the passage of gases through capillary tubes, and is more nearly analogous to the flow of a gas through a small hole in a thin plate.

When the diameter of the hole and the thickness of the plate are both small compared with the length of the free path of a molecule, then, as Sir WILLIAM THOMSON has shown, any molecule which comes up to the hole on either side will be in very little danger of encountering another molecule before it has got fairly through to the other side.

Hence the flow of gas in either direction through the hole will take place very nearly in the same manner as if there had been a vacuum on the other side of the hole, and this whether the gas on the other side of the hole is of the same or of a different kind.

If the gas on the two sides of the plate is of the same kind but at different temperatures, a phenomenon will take place which we may call *thermal effusion*.

The velocity of the molecules is proportional to the square root of the absolute temperature, and the quantity which passes out through the hole is proportional to this velocity and to the density. Hence, on whichever side the product of the density into the square root of the temperature is greatest, more molecules will pass from that side than from the other through the hole, and this will go on till this product is equal on both sides of the hole. Hence the condition of equilibrium is that the density must be inversely as the square root of the temperature, and since the pressure is as the product of the density into the temperature, the pressure will be directly proportional to the square root of the absolute temperature.

The theory of thermal effusion through a small hole in a thin plate is therefore a very simple one. It does not involve the theory of viscosity at all.

The finer the pores of a porous plate, and the rarer the gas which effuses through it, the more nearly does the passage of gas through the plate correspond to what we have called effusion, and the less does it depend on the viscosity of the gas.

The coarser the pores of the plate and the denser the gas, the further does the phenomenon depart from simple effusion, and the more nearly does it approach to transpiration through a capillary tube, which depends altogether on viscosity.

To return to the case of transpiration through a capillary tube. When the temperature is uniform

$$Q = -\frac{\pi \rho a^4}{8\mu} \frac{dp}{dz} \left(1 + 4\frac{G}{a}\right) \dots \dots \dots (78)$$

By experiments on capillary tubes of glass, MM. KUNDT and WARBURG found* for the value of G for air at different pressures and at from 17° C. to 27° C.,

$$G = \frac{8}{p} \text{ centimetres } \dots \dots \dots (79)$$

where p is the pressure in dynes per square centimetre, which is nearly the same as in millionths of an atmosphere. For hydrogen on glass

$$G = \frac{15}{p} \text{ centimetres } \dots \dots \dots (80)$$

When there is no flow of gas in a tube in which the temperature varies from end to end, the pressure is greater at the hot end than at the cold end. Putting Q=0 we have

$$\frac{dp}{d\theta} = 6 \frac{\mu^2}{\rho \theta} \frac{1}{a^2 + 4Ga} \dots \dots \dots (81)$$

The quantity $6 \frac{\mu^2}{\rho \theta}$ is just double of that calculated in section (3) of the introduction, and is therefore in C.G.S measure $0.63 \div p$ for dry air at 15° C. Let us suppose $a = 0.01$ centimetre, and the pressure 40 millimetres of mercury, then $G = 0.00016$ centimetre.

If one end of the tube is kept at 0° C. and the other at 100° C., the pressure at the hot end will exceed that at the cold end by about 1.2 millionths of an atmosphere.

The difference of pressure might be increased by using a tube of smaller bore and air of smaller density, but the effect is so small that though the theoretical proof of its existence seems satisfactory, an experimental verification of it would be difficult.

* Pogg. Ann., July, 1876.