-NOTES-

THE CONSERVATION OF SYSTEMS IN PHASE SPACE*

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1. Introduction. Important progress in the development of a statistical theory of the transport phenomena in liquids, based on the application of Gibbs' principle of "conservation of density-in-phase," has been made in recent papers by Kirkwood, by Born and Green, and by Jaffé. Kirkwood and Born and Green have derived the Maxwell-Boltzmann integro-differential equation and have developed a general statistical mechanical theory of transport processes, by application of the principle of continuity in phase space. In their method of treatment of this principle, Born and Green defined a set of multiform distribution functions and obtained a generalized equation of motion referring to a cluster of h molecules. This generalized equation reduces to the equation of motion of ordinary hydrodynamics when h=1. Born and Green also obtained expressions for the coefficients of thermal conductivity and of viscosity, but have not published any numerical results.

Using a method analogous to that introduced by Boltzmann⁵ in the kinetic theory of gases, Jaffé⁴ obtained a solution for the distribution function in the form of a multiple power series proceeding according to powers of the kinetic energy and resultant moments. Previously determined⁶ potential functions were used to calculate theoretical values for the coefficients of thermal conductivity and of viscosity of ten liquids. The numerical results obtained agree reasonably well with the observed values, in most instances.

In each of the three methods of treatment the consideration of boundary conditions has been almost completely avoided. Kirkwood and Born and Green have suggested making the distribution function vanish at the boundaries, and Jaffé limited his considerations to the neighborhood of a particle in the interior of the liquid. However, it would seem that, since the coefficients of heat conductivity and of viscosity are defined in terms of the transfer of thermal energy and of momentum through boundary surfaces, the theory of these dissipative processes cannot be considered as sufficiently well developed without the further consideration of boundary conditions. In our treatment of the principle of conservation of density-in-phase, the boundary conditions to

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¹J. Willard Gibbs, *Collected Works*, Longman, Green & Co., New York, 1931, Vol. II, Part I, "Elementary Principles in Statistical Mechanics," Ch. 1.

²J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946).

³M. Born and H. S. Green, Nature 159, 251 (1947); Proc. Roy. Soc. London (A) 188, 10 (1946), and subsequent papers.

⁴G. Jaffé, Phys. Rev. **69**, 688 (1946), **75**, 184 (1949).

⁵L. Boltzmann, Vorlesungen über Gastheorie, Johann A. Barth, 1896, 1. Theil, "Theorie der Gase mit einatomigen Molekülen, deren Dimensionen gegen die mittlere Weglänge verschwinden," p. 184.

⁶G. Jaffé, Phys. Rev. **62**, 463 (1942).

be applied refer to the boundaries of the region of phase space occupied by the systems of a virtual ensemble, rather than to the boundary condition problems as treated in hydrodynamics. The formulation of boundary conditions in phase space will be preceded by the statement of what may reasonably be assumed regarding boundary conditions in real space, in the most general case of a fluid contained in a finite volume V with moving boundaries.

A fluid system bounded by the walls of a container consists always of the same particles, but consideration of such a system is complicated by the presence of a boundary region of finite thickness where the particles of the fluid are in interaction with the molecules of the material comprising the walls. We may simplify the boundary conditions, in some respects, by considering a system which is entirely surrounded by a larger system of the same kind. Due to diffusion, the boundaries of the real system would become ill-defined if we were to require that the real system is to always consist of the same particles. We may, however, define the motion of the boundaries of the real system in such a way that, during any reasonably short interval of time, there is no mass current (see Eq. (2.12)) through the boundaries. During such an interval of time, there is no net diffusion of particles through the boundaries of the real system.

The analogy between the hydrodynamical fluid in real space and the imaginary fluid consisting of systems of the virtual ensemble in phase space may be extended by conceiving of a diffusion of the systems of the virtual ensemble. In order that the boundaries of the virtual ensemble should not become ill-defined, it is sufficient that the boundaries of the virtual ensemble should be defined in terms of the previously defined boundaries of the real system in real space. The boundary condition to be applied is that, during any reasonably short interval of time, there is no net diffusion of systems through the boundaries of the region of phase space occupied by the systems of the virtual ensemble. During such an interval of time, both the number of particles in the real system and the number of systems in the virtual ensemble remain constant.

In the present paper, boundary conditions of this very general nature will be applied in the derivation of an equation of transport analogous to the equations of transfer derived by Maxwell⁷ in his kinetic theory of gases. The ordinary equation of continuity, the hydrodynamical equations of motion, and the equations of thermal and of total energy will then be obtained as special cases of this general transport equation.

2. Preliminary definitions. We are considering a system of N identical particles, each of mass m. The state of the system at any instant is determined by the values of the 3N position coordinates (x_a, y_a, z_a) and of the corresponding momenta $(m(dx_a/dt), m(dy_a/dt), m(dz_a/dt))$ of the N particles. Let

$$q_{3a-2} = x_a$$
, $q_{3a-1} = y_a$, $q_{3a} = z_a$, $a = 1, 2, \dots N$, (2.1)

and

$$p_i = m \frac{dq_i}{dt}, \qquad i = 1, 2, \dots 3N.$$
 (2.2)

Then the 6N values of the q_i and the p_i at any instant determine a point in a 6N dimensional phase space. This point is representative of the instantaneous state of the

⁷J. C. Maxwell, Phil. Trans. 157, 1 (1886), or *Collected Works*, II, p. 26; J. H. Jeans, *The dynamical theory of gases*, The Univ. Press, Cambridge, 1925, Ch. IX.

system, and the progress of the system in time is represented by the motion of its representative point along a path in phase space. Following a method developed by Gibbs, we consider a virtual ensemble of \mathbf{N} such systems, each consisting of N identical particles, all of the systems being subject to the same internal and external forces, but distinguished in that they are distributed among the various states accessible to the actual system. In general, the ranges of the position coordinates q_i are determined by the physical volume occupied by the particles of the actual system. The ranges of the momentum coordinates p_i are limited by the maximum kinetic energy which the real system may have, but to avoid mathematical difficulties, we will follow the customary procedure by taking all real values for the ranges of the momentum coordinates

Letting

$$d\Omega_0 = \prod_{i=1}^{3N} dq_i dp_i \tag{2.3}$$

be the element of extension in phase space, we write

$$d\mathbf{N} = f(q, p, t) d\Omega_0 \tag{2.4}$$

for the number of systems in $d\Omega_0$ at time t. The distribution function f, which gives the instantaneous density of systems in phase space at the point (q, p), is in general a function of the 6N + 1 variables q, p, t. This function is subject to certain conditions analogous to the conditions first formulated by Hilbert⁸ for the distribution function of a gas in position-velocity space. In a strict sense, f is not a continuous function of the 6N + 1 variables. Nevertheless, it is assumed that the density of systems in phase space is so great that f can be approximated to a sufficient degree of accuracy by a function which is continuous and has continuous derivatives with respect to the phase coordinates and the time. Since a density is of necessity a positive quantity, the distribution function must not become negative within the ranges of these 6N + 1 variables. The distribution function must also be symmetrical in the phase coordinates of any two particles, inasmuch as any one of the N identical particles may be chosen as the representative particle. It is further assumed that the distribution function vanishes sufficiently rapidly, for large values of the momentum coordinates, to assure the existence of all integrals of the form $\int f \phi \ d\Omega_0$, where $\phi(q, p, t)$ is any polynomial in the momentum coordinates with coefficients continuous in the position coordinates and in the time.

The average value, $\langle \phi \rangle$, of a function ϕ of the phase coordinates and of the time, for a specified instant of time and for a specified position of a representative particle, say particle No. 1, is defined by

$$\langle \phi \rangle \int f \, d\Omega_1 = \int f \phi \, d\Omega_1 \,, \tag{2.5}$$

where

$$d\Omega_1 = \prod_{i=1}^{3N} dq_i \prod_{i=1}^{3N} dp_i$$
 (2.6)

is the element of extension in the subspace Ω_1 of Ω_0 . We note that Ω_1 is the section of Ω_0 obtained by assigning specified values to q_1 , q_2 , and q_3 . Selection of particle No. 1 as representative particle means that, henceforth, (q_1, q_2, q_3) may also be considered

⁸D. Hilbert, Math. Ann. 72, 562 (1912).

as the coordinates of a point in real space and need not be distinguished from (x_1, y_1, z_1) . From (2.5) and (2.6) it may be understood that $\langle \phi \rangle$ is, in general, a function of the four variables q_1 , q_2 , q_3 , and t even when ϕ itself does not depend explicitly on all four of these variables. This arises from the, in general, complicated manner in which the distribution function depends upon the position coordinates and on the time.

Letting

$$d\tau = dq_1 dq_2 dq_3 \tag{2.7}$$

be the element of extension in real space, and defining $d\mathbf{N}_1$ by

$$d\mathbf{N}_1 = d\tau \int f \, d\Omega_1 \,, \tag{2.8}$$

we may make the transformation to real space in the customary manner by writing

$$\frac{dN}{N} = \frac{d\mathbf{N}_1}{\mathbf{N}} \,, \tag{2.9}$$

where dN is the number of particles contained in $d\tau$ at a specified instant of time. Hence, by (2.8) and (2.9), the density n of particles in real space is given by

$$n = \frac{dN}{d\tau} = \frac{N}{\mathbf{N}} \int f \, d\Omega_1 \ . \tag{2.10}$$

We note from (2.5) and (2.10) that

$$\int f\phi \ d\Omega_1 = \frac{N}{\mathbf{N}} \, n\langle\phi\rangle \tag{2.11}$$

Letting i, j = 1, 2, or 3, the components mu_i of the mass current, the components S_{ij} of the strain tensor, the temperature T, and the components H_i of the heat current, at a specified instant of time and at a specified point (q_1, q_2, q_3) , are defined by

$$mu_i = \langle p_i \rangle, \tag{2.12}$$

$$S_{ij} = \frac{n}{m} \langle p_i' p_j' \rangle \tag{2.13}$$

$$3nkT = S_{11} + S_{22} + S_{33} , (2.14)$$

and

$$H_{i} = \frac{n}{2m^{2}} \langle p'_{i} \{ (p'_{i})^{2} + (p'_{2})^{2} + (p'_{3})^{2} \} \rangle$$
 (2.15)

respectively, where $p'_i = p_i - \langle p_i \rangle$.

3. The conservation of systems in phase space. If we define the operator D by

$$D = \frac{\partial}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{dq_i}{dt} \frac{\partial}{\partial q_i} + \frac{dp_i}{dt} \frac{\partial}{\partial p_i} \right\}, \tag{3.1}$$

the hydrodynamical equation of continuity in phase space assumes the form⁹

$$Df + f \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_i} \left(\frac{dq_i}{dt} \right) + \frac{\partial}{\partial p_i} \left(\frac{dp_i}{dt} \right) \right\} = 0.$$
 (3.2)

⁹Jeans, op. cit., p. 71.

The phase coordinates are connected by Hamilton's equations of motion,

$$\frac{dq_i}{dt} = \frac{\partial \epsilon}{\partial p_i}, \qquad \frac{dp_i}{dt} = \frac{-\partial \epsilon}{\partial q_i} + F_i, \qquad i = 1, 2, \dots 3N, \tag{3.3}$$

where ϵ is the Hamiltonian function for the system and the F_i are the components of non-conservative forces. Hereafter we shall, in most cases, designate the dp_i/dt by R_i . The forces whose components are the R_i may be partly of internal, partly of external origin. In case each force component R_i is independent of the corresponding momentum coordinate p_i , the 3N terms in the summation in (3.2) vanish and (3.2) leads to Gibbs' principle of conservation of density-in-phase, which is valid for non-conservative as well as for conservative systems, so long as $\partial R_i/\partial p_i = 0$.

When there is no diffusion of systems in phase space, the vanishing of the summation in (3.2) is equivalent to Gibbs' principle of extension-in-phase. This principle, together with Gibbs' principle of conservation of density-in-phase, would then imply conservation of the total number of systems in the virtual ensemble. However, when there is diffusion of systems in phase space, the motion in phase space of the boundary surface S_0 of Ω_0 is not determined by (3.3), and, in order to obtain conservation of the total number of systems in the virtual ensemble, we must supplement (3.2) by the boundary condition that there is no net flow of systems through the boundaries of the region of phase space available to the systems of the virtual ensemble. We proceed to give the mathematical formulation of this boundary condition, for the general case in which the boundary surface S_0 of Ω_0 is in motion in any arbitrary manner.

For complete generality, we consider a function $\psi = f\phi$ where ϕ is any polynomial in the momentum coordinates with coefficients which may be functions of the position coordinates and of the time. Then $\partial/\partial t \int \psi \ d\Omega_0$ is defined as the limit, as $\Delta t \to 0$, of the difference quotient of $\int \psi \ d\Omega_0$ evaluated at times t and $t + \Delta t$:

$$\frac{\partial}{\partial t} \int_{\Omega_0} \psi(q, p, t) d\Omega_0 = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left\{ \int_{\Omega_0} \psi(q, p, t + \Delta t) d\Omega_0 - \int_{\Omega_0} \psi(q, p, t) d\Omega_0 \right\}, \quad (3.4)$$

where Ω_0 and Ω'_0 are the regions of phase space occupied by the systems of the virtual ensemble at times t and $t + \Delta t$, respectively. Assuming that $\psi(q, p, t + \Delta t)$ may, for sufficiently small values of Δt , be expanded as a Maclaurin's series in Δt , we obtain, to terms of the first order in Δt ,

$$\int_{\Omega'_0} \psi(q, p, t + \Delta t) d\Omega_0 = \int_{\Omega'_0} \psi(q, p, t) d\Omega_0 + \Delta t \int_{\Omega_0} \frac{\partial \psi(q, p, t)}{\partial t} d\Omega_0. \quad (3.5)$$

Hence (3.4) becomes

$$\frac{\partial}{\partial t} \int_{\Omega_{\bullet}} \psi \, d\Omega_{0} = \int_{\Omega_{\bullet}} \frac{\partial \psi}{\partial t} \, d\Omega_{0} + \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_{\Omega'_{\bullet} - \Omega_{\bullet}} \psi \, d\Omega_{0} , \qquad (3.6)$$

where $\Omega'_0 - \Omega_0$ is the region of phase space through which the boundary surface S_0 of Ω_0 moves during time Δt . Letting $V_0(n)$ be the component of the velocity of motion of the element dS_0 of the boundary surface S_0 of Ω_0 , normal to dS_0 , we may write

$$d \Omega_0 = V_0(n) d S_0 \Delta t, \qquad (3.7)$$

where $d\Omega_0$ is the region of phase space through which dS_0 moves during time dt. Hence (3.6) becomes

$$\frac{\partial}{\partial t} \int_{\Omega_0} \psi \ d\Omega_0 = \int_{\Omega_0} \frac{\partial \psi}{\partial t} \ d\Omega_0 + \int_{S_0} \psi V_0(n) \ dS_0 \ . \tag{3.8}$$

We now let $v_0(n)$ be the component of the velocity of motion of a representative point at the surface element dS_0 of the surface S_0 of Ω_0 , normal to dS_0 . By Gauss' theorem for the transformation of a surface integral into a volume integral we may write

$$\int_{S_0} \psi v_0(n) \ dS_0 = \int_{\Omega_0} \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_i} \left(\psi \frac{dq_i}{dt} \right) + \frac{\partial}{dp_i} \left(\psi \frac{dp_i}{dt} \right) \right\} d\Omega_0 \ . \tag{3.9}$$

Upon combining (3.8) and (3.9), we obtain, by means of (3.1) and (3.4),

$$\frac{\partial}{\partial t} \int_{\Omega_{\bullet}} \psi \ d\Omega_{0} = \int_{\Omega_{\bullet}} \left[D\psi + \psi \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_{i}} \left(\frac{dq_{i}}{dt} \right) + \frac{\partial}{\partial p_{i}} \left(\frac{dp_{i}}{dt} \right) \right\} \right] d\Omega_{0}
+ \int_{S} \psi \{ V_{0}(n) - v_{0}(n) \} \ dS_{0} .$$
(3.10)

With $\psi = f$, we see that (3.10) states that the rate of increase of the total number of systems in the virtual ensemble is equal to the rate at which systems are produced in Ω_0 , augmented by the net rate of flow of systems into Ω_0 through its boundaries. In order to obtain conservation of the total number of systems in the virtual ensemble, we shall apply not only (3.2), but also the boundary condition that there is no net flow of systems through the boundaries of the region of phase space available to the systems of the virtual ensemble, so that the surface integral in (3.10) vanishes. We note that the surface integral in (3.10) may vanish without the integrand itself vanishing identically, that is, without $V_0(n) = v_0(n)$. For equality of these two generalized velocity components would imply that there is no transport of any quantity ϕ through the boundaries of the system. As a concrete example, we may consider the case of a fluid contained within rigid boundaries, with heat being applied at the boundaries. Then, to the extent that the walls are rigid, the boundaries of Ω_0 must also be considered as fixed, so that $V_0(n) = 0$. But, as there is transfer of heat into the system through the walls, the particles must, on the average, rebound from the walls with increased kinetic energy. This may be pictured in phase space by imagining that a system of the virtual ensemble flows out through the boundary of Ω_0 at the instant a particle strikes the rigid wall and another system flows in through the boundary when the particle rebounds from the wall, an infinitesimally short time later.

4. The equation of transport. An equation of transport, including the general case of moving boundaries, may be derived directly from (3.2) by the imposition of a boundary condition in the 6N-3 dimensional subspace Ω_1 of Ω_0 , analogous to the boundary condition previously imposed in Ω_0 . Let $V_1(n)$ be the component of the velocity of a point on the element dS_1 of the boundary surface S_1 of Ω_1 , normal to dS_1 , and let $v_1(n)$ be the component of the velocity of a representative point, in the subspace Ω_1 , at the moment that point is on or passes through dS_1 , normal to dS_1 . By exactly the same procedure as previously used, we obtain, corresponding to (3.8),

$$\frac{\partial}{\partial t} \int_{\Omega_1} \psi \ d\Omega_1 = \int_{\Omega_1} \frac{\partial \psi}{\partial t} \ d\Omega_1 + \int_{S_1} \psi V_1(n) \ dS_1 \ . \tag{4.1}$$

Since Ω_1 is the space of all 3N momentum coordinates but of only 3N-3 position coordinates, application of Gauss' theorem for the transformation of a surface integral into a volume integral gives

$$\int_{S_1} \psi v_1(n) \ dS_1 = \int_{\Omega_1} \left\{ \sum_{i=4}^{3N} \frac{\partial}{\partial q_i} \left(\psi \frac{dq_i}{dt} \right) + \sum_{i=1}^{3N} \frac{\partial}{\partial p_i} \left(\psi \frac{dp_i}{dt} \right) \right\} d\Omega_1 \ . \tag{4.2}$$

We now supply on both sides of (4.2) the three terms necessary to make the indices in both summations to run from 1 to 3N, combine the result with (4.1), replace ψ by $f\phi$, and apply (3.2) to obtain

$$\frac{\partial}{\partial t} \int_{\Omega_{1}} f \phi \ d\Omega_{1} + \sum_{i=1}^{3} \frac{\partial}{\partial q_{i}} \int f \frac{p_{i}}{m} \phi \ d\Omega_{1}$$

$$= \int_{\Omega_{1}} f \ D\phi \ d\Omega_{1} + \int_{S_{1}} f \phi \{ V_{1}(n) - v_{1}(n) \} \ dS_{1} . \tag{4.3}$$

When each member of (4.3) is multiplied by $N \Delta \tau / \mathbf{N}$, where $\Delta \tau$ is any fixed element of volume in real space, the first term on the left hand side of the resulting equation then represents the time rate of increase of the total amount of ϕ in $\Delta \tau$, and the summation represents the net rate of flow of the quantity ϕ out of $\Delta \tau$, through its boundaries. The first term on the right hand side, involving $D\phi$, then represents the rate of increase of the total amount of ϕ in $\Delta \tau$, due to the explicit dependence of ϕ on the phase coordinates and on the time. However, $V_1(n)$ and $v_1(n)$ are generalized velocity components in the imaginary subspace Ω_1 of phase space, and the surface integral over dS_1 , in the right hand side of (4.3), then represents the rate at which the quantity ϕ is transported into $\Delta \tau$, but not through its boundaries. The real physical space is a 3dimensional subspace of phase space, and there are paths in generalized coordinate space which lead from the exterior to the interior of the closed volume in real space, yet which do not pass through the boundaries of the real volume. As the transport of any physical quantity from the exterior to the interior of a closed volume, by a path not passing through its boundaries, is experimentally unobservable, we require that the surface integral in (4.3) shall vanish. We thus obtain a first form of the equation of transport:

$$\frac{\partial}{\partial t} \int f \phi \ d\Omega_1 + \sum_{i=1}^3 \frac{\partial}{\partial q_i} \int f \frac{p_i}{m} \phi \ d\Omega_1 = \int f(D\phi) \ d\Omega_1 \ , \tag{4.4}$$

which is valid for any quantity ϕ whose value for the entire system is equal to the sum of its values for the individual particles, and for which the integrals involved exist. A second form of the equation of transport (4.4) is readily obtained by the aid of (2.11):

$$\frac{\partial}{\partial t}\langle n\phi\rangle + \frac{1}{m}\sum_{i=1}^{3}\frac{\partial}{\partial q_{i}}\langle np_{i}\phi\rangle = n\langle D\phi\rangle, \tag{4.5}$$

since both N and \mathbf{N} are constant. The right hand side of (4.4), and of (4.5), remains to be developed, for any particular ϕ , by means of (3.1).

5. The equation of continuity, the equations of motion, and the energy equations. Letting $\phi = 1$, we obtain from (4.5), by means of (2.12),

$$\frac{\partial n}{\partial t} + \sum_{i=1}^{3} \frac{\partial}{\partial q_i} (nu_i) = 0, \qquad (5.1)$$

which is the equation of continuity. Elimination of $\partial n/\partial t$ from (4.5) and (5.1) results in a third form of the equation of transport:

$$\frac{d}{dt}\langle\phi\rangle + \frac{1}{nm}\sum_{i=1}^{3}\frac{\partial}{\partial q_{i}}\langle np'_{i}\phi\rangle = \langle D\phi\rangle, \tag{5.2}$$

where the operator d/dt is defined by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{i=1}^{3} u_i \frac{\partial}{\partial q_i}$$
 (5.3)

Letting $\phi = p_i$, $D\phi = R_i$, in (5.2), we obtain the hydrodynamical equations of motion,

$$\frac{d}{dt}(mu_i) + \frac{1}{n} \sum_{i=1}^{3} \frac{\partial S_{ij}}{\partial q_i} = \langle R_i \rangle, \qquad j = 1, 2, \text{ or } 3, \tag{5.4}$$

the components S_{ij} of the strain tensor having been defined in (2.13). We note that the mean force acting on the representative particle may be non-conservative even when the forces acting on the individual particles are conservative. Conservative internal forces may tend to increase or decrease the disordered motion of the particles composing the system, and this is interpreted, from the macroscopic point of view, as the effect of non-conservative forces acting on the parcels of the fluid, as in the appearance of tangential surface forces when there are velocity gradients.

In order to obtain the equation of thermal energy we may let $\phi = (1/2m) \sum_{i=1}^{3} (p_i')^2$ in (5.2). By the aid of (2.12) to (2.15) and of (3.1) we obtain

$$\frac{d}{dt}\left(\frac{3}{2}kT\right) + \frac{1}{n}\sum_{i=1}^{3}\frac{\partial H_{i}}{\partial a_{i}} + \frac{1}{n}\sum_{i=1}^{3}S_{ij}\frac{\partial u_{j}}{\partial a_{i}} = \frac{1}{m}\sum_{i=1}^{3}\langle R_{i}p_{i}'\rangle. \tag{5.5}$$

It is seen that external conservative forces, which depend at most on the position coordinates of the particle on which they act, and possibly on the time, make no contribution to the right hand side of (5.5). In the case of an ideal gas, whose internal energy is entirely kinetic, the right hand member of (5.5) vanishes. The resulting equation may then be compared with equation (13) of Enskog's dissertation.¹⁰ The terms in the right hand member of (5.5) become negligible in the case of a moderately dense gas for which the internal forces decay sufficiently rapidly with distance.

The equation of total energy may be obtained from (5.2) by letting $\phi = \epsilon_1 = \varphi_1^{(\epsilon)} + \varphi_1^{(i)} + (1/2m) (p_1^2 + p_2^2 + p_3^2)$, where $\varphi_1^{(\epsilon)}$ and $\varphi_1^{(i)}$ are the time independent external and internal potentials of the representative particle. The external potential $\varphi_1^{(\epsilon)}$ will be assumed to be a function of the position coordinates q_1 , q_2 , and q_3 of the representative particle only. Furthermore, only binary attractions and repulsions will be considered, so that the total potential of the entire system may be expressed as the sum of the po-

¹⁰D. Enskog, Kinetische Theorie der Vorgänge in mässig verdünnten Gasen, Inaugural Dissertation, Upsala, 1917, p. 18.

tentials of the individual particles. Upon substituting ϵ_1 for ϕ into (5.2), multiplying the resulting equation by n $d\tau$, and integrating over $d\tau$ at a constant time, we obtain, by the aid of (2.3), (2.6), (2.7), (2.11) to (2.15) and (3.1) to (3.3), and by considerations of symmetry,*

$$\frac{d}{dt} \int n\langle \epsilon_{i} \rangle d\tau + \int \sum_{i=1}^{3} \frac{\partial}{\partial q_{i}} \left(H_{i} + \sum_{i=1}^{3} S_{ii} u_{i} \right) d\tau + \int \sum_{i=1}^{3} \frac{\partial}{\partial q_{i}} \left\{ \frac{n}{m} \langle p_{i}' \varphi_{1}^{(i)} \rangle \right\} d\tau
= \int \sum_{i=1}^{3} \frac{n}{m} \langle p_{i} F_{i} \rangle d\tau,$$
(5.6)

where

$$\langle \epsilon_1 \rangle = \frac{1}{2} m(u_1^2 + u_2^2 + u_3^2) + \varphi_1^{(\epsilon)} + \langle \varphi_1^{(i)} \rangle + \frac{3}{2} kT.$$
 (5.7)

Upon transforming the second and third volume integrals on the left hand side of (5.6) into surface integrals, we see that this equation may be interpreted as stating that the time rate of increase of total energy of the system is equal to the rate at which the non-conservative body forces F_i and surface forces S_{ij} do work on the system, augmented by the rates of transport of thermal energy of disordered motion and of internal potential energy through its boundaries. The importance of this latter portion of the energy flux, arising from the strong intermolecular forces in the case of a liquid, has been pointed out by Born and Green.¹¹ This flux is not contained in the expression (2.15) for the components of the heat current.

NOTE ON THE HAMEL-SYNGE THEOREM*

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The theorem given by Synge¹ for a plane motion of a compressible viscous fluid is easily extended to a three dimensional motion.

Consider a compressible viscous fluid which moves inside a fixed closed surface B, on which the velocity vanishes. Our theorem is: A velocity $\mathbf{v}(x, y, z)$ is consistent with the foregoing boundary condition if and only if

$$\int_{\mathbf{v}} (\mathbf{A} \cdot \text{curl } \mathbf{v} - f \text{ div } \mathbf{v}) \, dx \, dy \, dz = 0, \tag{1}$$

^{*}In the equation obtained by letting $\phi = \epsilon_1$, in (5.2), we interchange the phase coordinates of the representative particle with those of each of the other N-1 particles in turn, and add the resulting equations. Then, by considerations of symmetry and by the aid of (2.3), (2.6), (2.7) and (2.11), $\int n \langle \epsilon_a \rangle d\tau = (N/\mathbf{N}) \int f \epsilon_a d\Omega_0 = (N/\mathbf{N}) \int f \epsilon_1 d\Omega_0 = \int n \langle \epsilon_1 \rangle d\tau$. A similar method of treatment applies to the other terms on the left hand side of the combined equation. The right hand side of this equation becomes $(N/\mathbf{N}) \int f(D\epsilon) d\Omega_0 = (N/\mathbf{N}) \int f \sum_{i=1}^{3N} (p_i F_i/m) d\Omega_0 = N \int \sum_{i=1}^{3} (m/n) \langle p_i F_i \rangle d\tau$, by the aid also of (3.2) and (3.3).

¹¹M. Born and H. S. Green, Proc. Roy. Soc. London (A) 190, 455 (1947).

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