in volume 57 of the *Annalen*, Professor Noble extends the results of Yoshiye by finding the necessary conditions that three or more equations of the form

$$F\left(x, y, z, \frac{\partial z}{\partial x}, \frac{\partial z}{\partial y}, \frac{\partial^2 z}{\partial x^2}, \frac{\partial^2 z}{\partial x \partial y}, \frac{\partial^2 z}{\partial y^2} \right) = 0$$

shall have solutions in common.

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NOTE ON STATISTICAL MECHANICS.

BY PROFESSOR EDWIN BIDWELL WILSON.

IN developing the elements of statistical mechanics it is customary though by no means essential to remark the analogy between that subject and hydromechanics.* The analogy arises primarily through the fact that the equation of continuity of hydrodynamics,

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad \text{or} \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0,$$

where u, v or u, v, w are the velocities in the fluid in two or in three dimensions, exists in the form

$$(1) \qquad \frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} = 0 \quad \text{or} \quad \sum_{i=1}^{i=n} \frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} = 0$$

for dynamical systems regulated by the hamiltonian canonical equations

$$(2) \qquad \dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (i = 1, 2, \cdots, n);$$

and it is further exemplified by connection of the Boltzmann-Larmor hydrodynamical interpretation of Jacobi's last multiplier with the principle of conservation of extension in phase.† The object of this note is to comment upon the analogy in question.

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* Jeans, The Dynamical Theory of Gases, p. 62. Gibbs, Elementary Principles in Statistical Mechanics, p. 11.

† Compare Whittaker, Analytical Dynamics, p. 272, and Gibbs, loc. cit., p. 29.

Let the $2n$ quantities $q_1, q_2, \cdots, q_n, p_1, p_2, \cdots, p_n$ be interpreted as rectangular coordinates in a space of $2n$ dimensions. And suppose that an ensemble of systems which satisfy (2) be imagined as distributed in that space with a density in phase D or with a probability in phase P which are functions of p_i, q_i, and the time t. Then, by the same reasoning as in hydromechanics, the density D or the probability P will satisfy the equation

$$\frac{dP}{dt} + P \sum_{i=1}^{i=n} \left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} \right) = \frac{dP}{dt} = 0.$$

As the condition for statistical equilibrium is that the density shall be independent of the time, it follows that for statistical equilibrium

$$\frac{\partial P}{\partial t} = - \sum_{i=1}^{i=n} \left(\frac{\partial P}{\partial p_i} \dot{p}_i + \frac{\partial P}{\partial q_i} \dot{q}_i \right) = 0.$$

These results are obtained with full discussion by Gibbs, loc. cit.

Suppose that the systems considered are specified by a single coordinate q and the momentum p. The connected hydrodynamical problem thus becomes two-dimensional. Let it be asked whether the fluid which represents the ensemble of systems is more fully comparable with the ordinary fluid of hydrodynamics than is implied by the existence of an analogue for the equation of continuity. In the first place it should be noted that the motion of the fictitious fluid is given by equations relating to its velocities, that is, by

$$\dot{q} = \frac{\partial H}{\partial p} = u(p, q), \quad \dot{p} = \frac{\partial H}{\partial q} = v(p, q).^*$$

If the velocities of a particle in ordinary dynamics be given, a differentiation with respect to the time will suffice to determine the forces. If the velocities in a continuous medium are given, the problem is not so simple. For suppose that

$$u = u(x, y) \quad \text{and} \quad v = v(x, y)$$

are the velocities in an ordinary fluid. Then

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* For convenience and definiteness it will be assumed throughout this note that H does not depend explicitly upon the time and moreover that H may be decomposed into the sum of the kinetic and potential energies.

$$\frac{du}{dt} = \frac{\partial u}{\partial x} u + \frac{\partial u}{\partial y} v + \frac{\partial u}{\partial t} = X - \frac{1}{\rho}\frac{\partial p}{\partial x},$$

$$\frac{dv}{dt} = \frac{\partial v}{\partial x} u + \frac{\partial V}{\partial y} v + \frac{\partial V}{\partial t} = Y - \frac{1}{\rho}\frac{\partial p}{\partial y},$$

where ρ is the density, p is the pressure, and X and Y are the components of the impressed forces per unit mass. It therefore appears that ρ and p may be assigned at pleasure and X, Y determined to suit.

To remove this indeterminateness, it might be required that the forces X, Y be derivable from a potential. Then $\dot{u}$ and $\dot{v}$, known functions of the variables, would afford the two equations

$$\dot{u} = -\frac{\partial V}{\partial x} - \frac{1}{\rho}\frac{\partial p}{\partial x}, \quad \dot{v} = -\frac{\partial V}{\partial y} - \frac{1}{\rho}\frac{\partial p}{\partial y}.$$

If ρ be constant, as in the dynamics of liquids, the problem is now impossible unless

$$\dot{u}dx + \dot{v}dy$$

is a perfect differential. On the other hand if ρ be not constant but a known function of the variables, the expression of the fact that

$$\left(\dot{u} + \frac{1}{\rho}\frac{\partial p}{\partial x}\right)dx + \left(\dot{v} + \frac{1}{\rho}\frac{\partial p}{\partial y}\right)dy$$

be a perfect differential will afford a partial differential equation from which p may be determined. It should be remembered, however, that in the case of any real fluid, there is generally assumed an equation $F(p, \rho, T) = 0$ connecting the pressure, density, and temperature. The temperature is generally disregarded for purposes of hydrodynamics and it is assumed that $F(p, \rho) = 0$. The determination of p by the method suggested above would not generally give a result in which p was a function of ρ. In fact if p is a function of ρ, the equations may be written as

$$\dot{u} = -\frac{\partial V}{\partial x} - \frac{\partial \bar{p}}{\partial x}, \quad \dot{v} = -\frac{\partial V}{\partial y} - \frac{\partial \bar{p}}{\partial y}, \quad \bar{p} = \int \frac{dp}{\rho}$$

and the problem would again generally be impossible.

With these points in connection with the purely hydrodynamical problem in mind we may return to the matter of statistical mechanics and ask in the first place what are the conditions that there should be a velocity potential for the motion of the fictitious fluid.   If, when there is only one variable,

$$\dot{q}dq + \dot{p}dp = \frac{\partial H}{\partial p}dq - \frac{\partial H}{\partial q}dp$$

is a perfect differential, the expression

$$\Delta H = \frac{\partial^2 H}{\partial p^2} + \frac{\partial^2 H}{\partial q^2} = 0.$$

Now by hypothesis, H is of the second order in p.   Hence

$$\frac{\partial^3 H}{\partial p^3} + \frac{\partial^3 H}{\partial p \partial q^2} = 0 \quad \text{gives} \quad \frac{\partial^3 H}{\partial p^3} = \frac{\partial^3 H}{\partial p \partial q^2} = 0.$$

The differentiation with respect to p and q to find the derivatives of the fourth order shows at once that

$$\frac{\partial^4 H}{\partial p^4} = \frac{\partial^4 H}{\partial p^3 \partial q} = \frac{\partial^4 H}{\partial p^2 \partial q^2} = \frac{\partial^4 H}{\partial q^4} = 0.$$

Hence H is a polynomial of at most the third degree in p and q.

If there had been more variables, say two, the conditions that

$$\frac{\partial H}{\partial p_1}dq_1 - \frac{\partial H}{\partial q_1}dp_1 + \frac{\partial H}{\partial p_2}dq_2 - \frac{\partial H}{\partial p_2}dp_2$$

be a perfect differential would be

$$\frac{\partial^2 H}{\partial p_1^2} + \frac{\partial^2 H}{\partial q_1^2} = 0, \qquad \frac{\partial^2 H}{\partial p_2^2} + \frac{\partial^2 H}{\partial q_2^2} = 0,$$

$$\frac{\partial^2 H}{\partial p_1 \partial p_2} + \frac{\partial^2 H}{\partial q_1 \partial q_2} = 0, \quad \frac{\partial^2 H}{\partial p_1 \partial q_2} = \frac{\partial^2 H}{\partial p_2 \partial q_1} = 0,$$

and in a similar manner would show that H must be a polynomial of at most the third degree in p_i and q_i jointly.   The result is the same for any number of variables.   Hence it appears that only in a very restricted type of cases can there exist a velocity potential for the fictitious fluid, namely, when H, being of the second degree in p_i, is at most of the third

degree in p_i and q_i jointly, and even in this case there are still certain relations to be satisfied by the coefficients of the polynomial H. In such cases only would a velocity potential exist for the fictitious motion.

Let it now be asked whether the equations

$$q = -\frac{\partial V}{\partial q} - \frac{1}{P}\frac{\partial \Pi}{\partial q}, \quad \ddot{p} = -\frac{\partial V}{\partial p} - \frac{1}{P}\frac{\partial \Pi}{\partial p},$$

where P is the probability in phase and Π is a fictitious pressure for the fictitious fluid, can be satisfied. In the first place it may be noted that

$$\ddot{q} = \frac{d}{dt}\frac{\partial H}{\partial p} = \frac{\partial^2 H}{\partial q \partial p}\frac{\partial H}{\partial p} - \frac{\partial^2 H}{\partial p^2}\frac{\partial H}{\partial q} = -J\left(H, \frac{\partial H}{\partial p}\right),$$

$$\ddot{p} = -\frac{d}{dt}\frac{\partial H}{\partial q} = -\frac{\partial^2 H}{\partial q^2}\frac{\partial H}{\partial p} + \frac{\partial^2 H}{\partial q \partial p}\frac{\partial H}{\partial q} = J\left(H, \frac{\partial H}{\partial q}\right),$$

where J denotes the jacobian with respect to q and p of the quantities in the parenthesis. The equations to be satisfied are therefore

$$-J\left(H, \frac{\partial H}{\partial p}\right) + \frac{1}{P}\frac{\partial \Pi}{\partial q} = -\frac{\partial V}{\partial q},$$

$$J\left(H, \frac{\partial H}{\partial q}\right) + \frac{1}{P}\frac{\partial \Pi}{\partial p} = -\frac{\partial V}{\partial p}.$$

The equation obtained by differentiating these expressions respectively with respect to p and q and subtracting is seen at once to be simply

$$(3) \qquad\qquad J(H, \Delta H) = J(\Pi, P^{-1}).$$

This is a partial differential equation of the first order and first degree in Π which will in general suffice to determine Π when P is known.

The form of (3) is such that one interesting theorem is obvious : The necessary and sufficient condition that there may be a functional relation $F(\Pi, P) = 0$ between the pressure and density in the fictitious fluid is that the function H satisfy the relation

$$\Delta H = \frac{\partial^2 H}{\partial p^2} + \frac{\partial^2 H}{\partial q^2} = \Phi(H),$$

where Φ is any function of H. In this case $\ddot{q}\,dq + \ddot{p}\,dp$ is a perfect differential and the complete integration of the differential may be found.

$$\int \left(\frac{\partial^2 H}{\partial q \partial p} \frac{\partial H}{\partial p} - \frac{\partial^2 H}{\partial p^2}\cdot\frac{\partial H}{\partial q} \right) dq + \left(\frac{\partial^2 H}{\partial q \partial p} \frac{\partial H}{\partial q} - \frac{\partial^2 H}{\partial q^2} \frac{\partial H}{\partial p} \right) dp =$$

$$\frac{1}{2}\left[\left(\frac{\partial H}{\partial p}\right)^2 + \left(\frac{\partial H}{\partial q}\right)^2 \right] - \int \Phi(H)\,dH = -\,V - \bar{\bar{\Pi}},$$

where

$$\bar{\bar{\Pi}} = \int \frac{d\Pi}{P} = \int \frac{d\Pi}{dH}\frac{dH}{P}.$$

It therefore appears natural to take the functions V and Π as

$$V = -\tfrac{1}{2}\left[\left(\frac{\partial H}{\partial p}\right)^2 + \left(\frac{\partial H}{\partial q}\right)^2 \right], \quad \Pi = \int P\,\Phi(H)dH.^*$$

Here P may be any function of H which satisfies the necessary relation

$$\int\int P dp dq = 1 \quad \text{(within limits considered)},$$

although there is a large family of functions defined by such a general relation as $\Delta H = \Phi(H)$. The fact that H is necessarily quadratic in p suffices, as in the case of $\Delta H = 0$, to determine H except for a few arbitrary constants of integration. In fact, under the assumption that H is divisible into a kinetic and a potential energy,

$$H = \tfrac{1}{2}f(q)p^2 - \phi(q), \quad \Delta H = f(q) + \tfrac{1}{2}f''(q)p^2 - \phi''(q),$$

$$J(H, \Delta H) = \begin{vmatrix} \tfrac{1}{2}f'(q)p^2 - \phi'(q) & f(q)p \\ f'(q) + \tfrac{1}{2}f'''(q)p^2 - \phi'''(q) & f''(q)p \end{vmatrix} \equiv 0,$$

and hence

$$f(q)f'''(q) - f''(q)f'(q) = 0,$$

$$f(q)[f'(q) - \phi'''(q)] + f''(q)\phi'(q) = 0.$$

The first of these equations gives $f'' = kf$ and the second reduces to

$$f'(q) - \phi'''(q) + k\phi'(q) = 0.$$

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*This choice seems the simplest; but any function of H may be added to Π and a compensating change introduced in V.

The complete determination of f then gives the results

$$f = aq + b, \quad f = a \cos (\sqrt{-k}q + b), \quad f = a e^{\sqrt{k}q} + b c^{-\sqrt{k}q},$$

according as k is zero, negative or positive. The determination of $\phi(q)$ then calls for the solution of a linear equation with constant coefficients and with second member. The class of problems of mechanics which result from such a value of H is somewhat restricted. In case the coordinate q is so chosen that $f(q) = \text{const}, \phi'''(q) = 0$; and the potential energy is a quadratic in q — a very restricted but well known and frequently occurring type of problem.*

To return to the general case, $J(H, \Delta H) \neq 0$. Here the equation (3) will determine Π when P is given. As there is only one variable, there is only one invariant of the motion of any given one of the systems in the ensemble, and that invariant is H. For statistical equilibrium, it is therefore necessary that P shall be a function of H. As H and ΔH are functionally independent, they may be taken as the independent variables, and by the rules of operation with jacobians,

$$1 = \frac{J(\Pi, P^{-1})}{J(H, \Delta H)} = \begin{vmatrix} \dfrac{\partial \Pi}{\partial \Delta} & \dfrac{\partial P^{-1}}{\partial H} \\[2mm] \dfrac{\partial \Pi}{\partial \Delta H} & \dfrac{\partial P^{-1}}{\partial \Delta H} \end{vmatrix}$$

Hence for statistical equilibrium this result becomes merely

$$\frac{dP^{-1}}{dH} \frac{\partial \Pi}{\partial \Delta H} = -1, \quad \Pi = -\frac{dH}{dP^{-1}} \Delta H + f(H).\dagger$$

The expression for Π is determined except for an additive arbitrary function of H. No more complete determination could be expected because the fictitious potential V may take on an additive function of H.

For simplicity it may be assumed that the additive function $f(H)$ is omitted from Π. The determination of V is then straightforward and simple. In fact

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* It may be noted that if $\Delta H = 0$ in this case, the potential energy is $-\phi(q) = -\frac{1}{2}f(q)q^2 + mq + n$, where $f(q)$ is a constant necessarily positive. The force is therefore repulsive, and Gibbs's canonical distribution would be illusory. See Gibbs, loc. cit., p. 35.

† This expression which is of the form $\Pi = \phi(P)\Delta H + \psi(P)$ corresponds to the equation $F(p, \rho, T) = 0$ of ordinary fluids. In a way, therefore, it may be said that ΔH corresponds to T.

$$V = P^{-1}\Delta H \frac{dH}{dP^{-1}} - \frac{1}{2}\left[\left(\frac{\partial H}{\partial p}\right)^2 + \left(\frac{\partial H}{\partial q}\right)^2\right]$$

With this value of V and the value for Π obtained above the equations of the fictitious fluid become identical with those of a real fluid. The values of V and Π may further be written as

$$V = -\Delta H \frac{dH}{d\eta} - \frac{1}{2}\left[\left(\frac{\partial H}{\partial p}\right)^2 + \left(\frac{\partial H}{\partial q}\right)^2\right],$$

$$\Pi = e^{\eta}\Delta H \frac{dH}{d\eta}, \quad \text{where } \eta = \log P$$

is the index of probability in phase. As e^{η} is necessarily positive, $\Delta H \cdot dH/d\eta$ must be always positive if Π is to be positive, as in the case of a real fluid. In the case of Gibbs's canonical distribution

$$P = e^{\frac{\psi - H}{\Theta}}, \quad \eta = \frac{\psi - H}{\Theta}$$

and $d\eta/dH$ is negative. For simple vibrating systems ΔH is positive * and hence for these systems Π would be negative and represent a tension.

The difficulty that Π is frequently negative may be remedied in some cases by a proper choice of the additive function $f(H)$. This, however, complicates the formulas and is not particularly desirable. In fact if the fictitious medium tended to expand, the concept of statistical equilibrium would be difficult of application. On the whole, the hydrodynamic analogy does not appear to be as close and vital as could be desired when developed to a greater extent than is implied in the equation (1) of continuity, although tolerably satisfactory results have been obtained for the case $n = 1$. When the number of variables n is greater than one, the $2n$ equations

$$\ddot{q}_i = -\frac{\partial V}{\partial q_i} - \frac{1}{P}\frac{\partial \Pi}{\partial q_i}, \quad \ddot{p}_i = -\frac{\partial V}{\partial p_i} - \frac{1}{P}\frac{\partial \Pi}{\partial p_i}$$

cannot be satisfied except under extremely restricted hypotheses concerning H. The conditions that the expression

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* For instance when $H = \frac{1}{2}p^2 + \frac{1}{2}n^2q^2 + kq^4$. If the system is that of harmonic vibrations, ΔH is constant, $J(H, \Delta H) = 0$, and the system comes under a previous type.

$$\Sigma \left(\dot{q}_i + \frac{1}{P}\frac{\partial \Pi}{\partial q_i} \right) dq_i + \Sigma \left(\dot{p}_i + \frac{1}{P}\frac{\partial \Pi}{\partial p_i} \right) dp_i = - \, dV$$

are too numerous to be satisfied by any functions P, Π, V. It is, however, possible that a medium, which satisfies the equation of continuity (1) and has equations more complicated than the hydromechanical type, some elastic medium, may be found to answer the purposes of the problem.

From a physical point of view, however, there is one matter which is of serious disadvantage in any hydrodynamical interpretation of the problem of statistical mechanics. That is the question of dimensions. If v denote the velocity in the fictitious fluid, then

$$v^2 = \dot{q}_1^2 + \dot{p}_1^2 + \dot{q}_2^2 + \dot{p}_2^2 + \cdots$$

is without physical significance unless the dimensions of q_1, q_2, $\cdots$, p_1, p_2, $\cdots$ are all alike. But the very equations (2) defining q_i, p_i, give

$$[\dot{q}_i] = \frac{[H]}{[p_i]}, \quad [\dot{p}_i] = \frac{[H]}{[q_i]}, \quad [p_i q_i] = [H], \quad [p_i] = [q_i],$$

where the brackets are used as dimensional symbols. Hence the dimensions are

$$[p_i] = [q_i] = [m]^{\frac{1}{2}} \frac{[l]}{[t]} .$$

where m, l, t denote mass, distance, time. As p_i and q_i seldom, if ever, have such dimensions as are here required, v^2 is not a physical quantity. The same is true of ΔH. It is interesting to note that the equation of continuity is such that its dimensionality is always $[t]^{-1}$, as it should be.

The importance of the homogeneity of physical dimensions of formulas is so great and mathematical investigations and analysis carried on without due regard to dimensions are so seldom of physical importance, that despite the results obtained for $n = 1$, the above considerations suggest the improbability of finding any continuous medium which shall properly shadow forth the relations of statistical mechanics. Otherwise it would be tempting to try to find such media for the cases where $n \geqq 2$. That which replaces the detailed physical concept of a medium is the mathematical concept of integral invariants, and these are dimensionally homogeneous.

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