ELEMENTARY PRINCIPLES IN STATISTICAL MECHANICS

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CHAPTER I.

GENERAL NOTIONS. THE PRINCIPLE OF CONSERVATION OF EXTENSION-IN-PHASE.

We shall use Hamilton's form of the equations of motion for a system of n degrees of freedom, writing $q_1, \ldots q_n$ for the (generalized) coördinates, $\dot{q}_1, \ldots \dot{q}_n$ for the (generalized) velocities, and

$$F_1\, dq_1 + F_2\, dq_2 \ldots + F_n\, dq_n \qquad (1)$$

for the moment of the forces. We shall call the quantities $F_1, \ldots F_n$ the (generalized) forces, and the quantities $p_1 \ldots p_n$, defined by the equations

$$p_1 = \frac{d\epsilon_p}{d\dot{q}_1}, \quad p_2 = \frac{d\epsilon_p}{d\dot{q}_2}, \quad \text{etc.,} \qquad (2)$$

where ϵ_p denotes the kinetic energy of the system, the (generalized) momenta. The kinetic energy is here regarded as a function of the velocities and coördinates. We shall usually regard it as a function of the momenta and coördinates,* and on this account we denote it by ϵ_p. This will not prevent us from occasionally using formulæ like (2), where it is sufficiently evident the kinetic energy is regarded as function of the $\dot{q}$'s and q's. But in expressions like $d\epsilon_p/dq_1$, where the denominator does not determine the question, the kinetic

* The use of the momenta instead of the velocities as independent variables is the characteristic of Hamilton's method which gives his equations of motion their remarkable degree of simplicity. We shall find that the fundamental notions of statistical mechanics are most easily defined, and are expressed in the most simple form, when the momenta with the coördinates are used to describe the state of a system.

energy is always to be treated in the differentiation as function of the p's and q's.

We have then

$$\dot{q}_1 = \frac{d\epsilon_p}{dp_1}, \quad \dot{p}_1 = -\frac{d\epsilon_p}{dq_1} + F_1, \quad \text{etc.} \tag{3}$$

These equations will hold for any forces whatever. If the forces are conservative, in other words, if the expression (1) is an exact differential, we may set

$$F_1 = -\frac{d\epsilon_q}{dq_1}, \quad F_2 = -\frac{d\epsilon_q}{dq_2}, \quad \text{etc.,} \tag{4}$$

where ϵ_q is a function of the coördinates which we shall call the potential energy of the system. If we write ϵ for the total energy, we shall have

$$\epsilon = \epsilon_p + \epsilon_q, \tag{5}$$

and equations (3) may be written

$$\dot{q}_1 = \frac{d\epsilon}{dp_1}, \quad \dot{p}_1 = -\frac{d\epsilon}{dq_1}, \quad \text{etc.} \tag{6}$$

The potential energy (ϵ_q) may depend on other variables beside the coördinates $q_1 \ldots q_n$. We shall often suppose it to depend in part on coördinates of external bodies, which we shall denote by a_1, a_2, etc. We shall then have for the complete value of the differential of the potential energy *

$$d\epsilon_q = -F_1\, dq_1 \ldots - F_n\, dq_n - A_1\, da_1 - A_2\, da_2 - \text{etc.,} \tag{7}$$

where A_1, A_2, etc., represent forces (in the generalized sense) exerted by the system on external bodies. For the total energy (ϵ) we shall have

$$d\epsilon = \dot{q}_1\, dp_1 \ldots + \dot{q}_n\, dp_n - \dot{p}_1\, dq_1 \ldots \\ - \dot{p}_n\, dq_n - A_1\, da_1 - A_2\, da_2 - \text{etc.} \tag{8}$$

It will be observed that the kinetic energy (ϵ_p) in the most general case is a quadratic function of the p's (or $\dot{q}$'s)

* It will be observed, that although we call ϵ_q the potential energy of the system which we are considering, it is really so defined as to include that energy which might be described as mutual to that system and external bodies.

involving also the q's but not the a's; that the potential energy, when it exists, is function of the q's and a's; and that the total energy, when it exists, is function of the p's (or $\dot{q}$'s), the q's, and the a's. In expressions like $d\epsilon/dq_1$, the p's, and not the $\dot{q}$'s, are to be taken as independent variables, as has already been stated with respect to the kinetic energy.

Let us imagine a great number of independent systems, identical in nature, but differing in phase, that is, in their condition with respect to configuration and velocity. The forces are supposed to be determined for every system by the same law, being functions of the coördinates of the system $q_1, \ldots q_n$, either alone or with the coördinates a_1, a_2, etc. of certain external bodies. It is not necessary that they should be derivable from a force-function. The external coördinates a_1, a_2, etc. may vary with the time, but at any given time have fixed values. In this they differ from the internal coördinates $q_1, \ldots q_n$, which at the same time have different values in the different systems considered.

Let us especially consider the number of systems which at a given instant fall within specified limits of phase, viz., those for which

$$\left.\begin{array}{ll} p_1' < p_1 < p_1'', & q_1' < q_1 < q_1'', \\ p_2' < p_2 < p_2'', & q_2' < q_2 < q_2'', \\ \cdots\cdots & \cdots\cdots \\ p_n' < p_n < p_n'', & q_n' < q_n < q_n'', \end{array}\right\} \qquad (9)$$

the accented letters denoting constants. We shall suppose the differences $p_1'' - p_1'$, $q_1'' - q_1'$, etc. to be infinitesimal, and that the systems are distributed in phase in some continuous manner,* so that the number having phases within the limits specified may be represented by

$$D\,(p_1'' - p_1') \ldots (p_n'' - p_n')\,(q_1'' - q_1') \ldots (q_n'' - q_n'), \qquad (10)$$

* In strictness, a finite number of systems cannot be distributed continuously in phase. But by increasing indefinitely the number of systems, we may approximate to a continuous law of distribution, such as is here described. To avoid tedious circumlocution, language like the above may be allowed, although wanting in precision of expression, when the sense in which it is to be taken appears sufficiently clear.

or more briefly by

$$D\, dp_1 \ldots dp_n\, dq_1 \ldots dq_n, \tag{11}$$

where D is a function of the p's and q's and in general of t also, for as time goes on, and the individual systems change their phases, the distribution of the ensemble in phase will in general vary. In special cases, the distribution in phase will remain unchanged. These are cases of *statistical equilibrium*.

If we regard all possible phases as forming a sort of extension of $2n$ dimensions, we may regard the product of differentials in (11) as expressing an element of this extension, and D as expressing the density of the systems in that element. We shall call the product

$$dp_1 \ldots dp_n\, dq_1 \ldots dq_n \tag{12}$$

an element of *extension-in-phase*, and D the *density-in-phase* of the systems.

It is evident that the changes which take place in the density of the systems in any given element of extension-in-phase will depend on the dynamical nature of the systems and their distribution in phase at the time considered.

In the case of conservative systems, with which we shall be principally concerned, their dynamical nature is completely determined by the function which expresses the energy (ϵ) in terms of the p's, q's, and a's (a function supposed identical for all the systems); in the more general case which we are considering, the dynamical nature of the systems is determined by the functions which express the kinetic energy (ϵ_p) in terms of the p's and q's, and the forces in terms of the q's and a's. The distribution in phase is expressed for the time considered by D as function of the p's and q's. To find the value of dD/dt for the specified element of extension-in-phase, we observe that the number of systems within the limits can only be varied by systems passing the limits, which may take place in $4n$ different ways, viz., by the p_1 of a system passing the limit p_1', or the limit p_1'', or by the q_1 of a system passing the limit q_1', or the limit q_1'', etc. Let us consider these cases separately.

In the first place, let us consider the number of systems which in the time dt pass into or out of the specified element by p_1 passing the limit p_1'. It will be convenient, and it is evidently allowable, to suppose dt so small that the quantities $\dot{p}_1\, dt$, $\dot{q}_1\, dt$, etc., which represent the increments of p_1, q_1, etc., in the time dt shall be infinitely small in comparison with the infinitesimal differences $p_1'' - p_1'$, $q_1'' - q_1'$, etc., which determine the magnitude of the element of extension-in-phase. The systems for which p_1 passes the limit p_1' in the interval dt are those for which at the commencement of this interval the value of p_1 lies between p_1' and $p_1' - \dot{p}_1\, dt$, as is evident if we consider separately the cases in which $\dot{p}_1$ is positive and negative. Those systems for which p_1 lies between these limits, and the other p's and q's between the limits specified in (9), will therefore pass into or out of the element considered according as $\dot{p}$ is positive or negative, unless indeed they also pass some other limit specified in (9) during the same interval of time. But the number which pass any two of these limits will be represented by an expression containing the square of dt as a factor, and is evidently negligible, when dt is sufficiently small, compared with the number which we are seeking to evaluate, and which (with neglect of terms containing dt^2) may be found by substituting $\dot{p}_1\, dt$ for $p_1'' - p_1'$ in (10) or for dp_1 in (11).

The expression

$$D\, \dot{p}_1\, dt\, dp_2 \ldots dp_n\, dq_1 \ldots dq_n \tag{13}$$

will therefore represent, according as it is positive or negative, the increase or decrease of the number of systems within the given limits which is due to systems passing the limit p_1'. A similar expression, in which however D and $\dot{p}$ will have slightly different values (being determined for p_1'' instead of p_1'), will represent the decrease or increase of the number of systems due to the passing of the limit p_1''. The difference of the two expressions, or

$$\frac{d(D\,\dot{p}_1)}{dp_1}\, dp_1 \ldots dp_n\, dq_1 \ldots dq_n\, dt \tag{14}$$

will represent algebraically the decrease of the number of systems within the limits due to systems passing the limits p_1' and p_1''.

The decrease in the number of systems within the limits due to systems passing the limits q_1' and q_1'' may be found in the same way. This will give

$$\left(\frac{d(D\dot{p}_1)}{dp_1} + \frac{d(D\dot{q}_1)}{dq_1}\right) dp_1 \ldots dp_n\, dq_1 \ldots dq_n\, dt \tag{15}$$

for the decrease due to passing the four limits p_1', p_1'', q_1', q_1''. But since the equations of motion (3) give

$$\frac{d\dot{p}_1}{dp_1} + \frac{d\dot{q}_1}{dq_1} = 0, \tag{16}$$

the expression reduces to

$$\left(\frac{dD}{dp_1}\dot{p}_1 + \frac{dD}{dq_1}\dot{q}_1\right) dp_1 \ldots dp_n\, dq_1 \ldots dq_n\, dt. \tag{17}$$

If we prefix Σ to denote summation relative to the suffixes $1 \ldots n$, we get the total decrease in the number of systems within the limits in the time dt. That is,

$$\Sigma \left(\frac{dD}{dp_1}\dot{p}_1 + \frac{dD}{dq_1}\dot{q}_1\right) dp_1 \ldots dp_n\, dq_1 \ldots dq_n\, dt = \\ - dD\, dp_1 \ldots dp_n\, dq_1 \ldots dq_n, \tag{18}$$

or

$$\left(\frac{dD}{dt}\right)_{p,q} = - \Sigma \left(\frac{dD}{dp_1}\dot{p}_1 + \frac{dD}{dq_1}\dot{q}_1\right), \tag{19}$$

where the suffix applied to the differential coefficient indicates that the p's and q's are to be regarded as constant in the differentiation. The condition of statistical equilibrium is therefore

$$\Sigma \left(\frac{dD}{dp_1}\dot{p}_1 + \frac{dD}{dq_1}\dot{q}_1\right) = 0. \tag{20}$$

If at any instant this condition is fulfilled for all values of the p's and q's, $(dD/dt)_{p,q}$ vanishes, and therefore the condition will continue to hold, and the distribution in phase will be permanent, so long as the external coördinates remain constant. But the statistical equilibrium would in general be disturbed by a change in the values of the external coördinates, which would alter the values of the $\dot{p}$'s as determined by equations (3), and thus disturb the relation expressed in the last equation.

If we write equation (19) in the form

$$\left(\frac{dD}{dt}\right)_{p,q} dt + \Sigma \left(\frac{dD}{dp_1} \dot{p}_1\, dt + \frac{dD}{dq_1} \dot{q}_1\, dt\right) = 0, \tag{21}$$

it will be seen to express a theorem of remarkable simplicity. Since D is a function of t, $p_1, \ldots p_n$, $q_1, \ldots q_n$, its complete differential will consist of parts due to the variations of all these quantities. Now the first term of the equation represents the increment of D due to an increment of t (with constant values of the p's and q's), and the rest of the first member represents the increments of D due to increments of the p's and q's, expressed by $\dot{p}_1\, dt$, $\dot{q}_1\, dt$, etc. But these are precisely the increments which the p's and q's receive in the movement of a system in the time dt. The whole expression represents the total increment of D for the varying phase of a moving system. We have therefore the theorem:—

*In an ensemble of mechanical systems identical in nature and subject to forces determined by identical laws, but distributed in phase in any continuous manner, the density-in-phase is constant in time for the varying phases of a moving system; provided, that the forces of a system are functions of its coördinates, either alone or with the time.**

This may be called the principle of *conservation of density-in-phase.* It may also be written

$$\left(\frac{dD}{dt}\right)_{a, \ldots h} = 0, \tag{22}$$

where $a, \ldots h$ represent the arbitrary constants of the integral equations of motion, and are suffixed to the differential co-

* The condition that the forces $F_1, \ldots F_n$ are functions of $q_1, \ldots q_n$ and a_1, a_2, etc., which last are functions of the time, is analytically equivalent to the condition that $F_1, \ldots F_n$ are functions of $q_1, \ldots q_n$ and the time. Explicit mention of the external coördinates, a_1, a_2, etc., has been made in the preceding pages, because our purpose will require us hereafter to consider these coördinates and the connected forces, A_1, A_2, etc., which represent the action of the systems on external bodies.

efficient to indicate that they are to be regarded as constant in the differentiation.

We may give to this principle a slightly different expression. Let us call the value of the integral

$$\int \dots \int dp_1 \dots dp_n \, dq_1 \dots dq_n \tag{23}$$

taken within any limits the *extension-in-phase* within those limits.

When the phases bounding an extension-in-phase vary in the course of time according to the dynamical laws of a system subject to forces which are functions of the coördinates either alone or with the time, the value of the extension-in-phase thus bounded remains constant. In this form the principle may be called the principle of *conservation of extension-in-phase.* In some respects this may be regarded as the most simple statement of the principle, since it contains no explicit reference to an ensemble of systems.

Since any extension-in-phase may be divided into infinitesimal portions, it is only necessary to prove the principle for an infinitely small extension. The number of systems of an ensemble which fall within the extension will be represented by the integral

$$\int \dots \int D \, dp_1 \dots dp_n \, dq_1 \dots dq_n.$$

If the extension is infinitely small, we may regard D as constant in the extension and write

$$D \int \dots \int dp_1 \dots dp_n \, dq_1 \dots dq_n$$

for the number of systems. The value of this expression must be constant in time, since no systems are supposed to be created or destroyed, and none can pass the limits, because the motion of the limits is identical with that of the systems. But we have seen that D is constant in time, and therefore the integral

$$\int \dots \int dp_1 \dots dp_n \, dq_1 \dots dq_n,$$

which we have called the extension-in-phase, is also constant in time.*

Since the system of coördinates employed in the foregoing discussion is entirely arbitrary, the values of the coördinates relating to any configuration and its immediate vicinity do not impose any restriction upon the values relating to other configurations. The fact that the quantity which we have called density-in-phase is constant in time for any given system, implies therefore that its value is independent of the coördinates which are used in its evaluation. For let the density-in-phase as evaluated for the same time and phase by one system of coördinates be D_1', and by another system D_2'. A system which at that time has that phase will at another time have another phase. Let the density as calculated for this second time and phase by a third system of coördinates be D_3''. Now we may imagine a system of coördinates which at and near the first configuration will coincide with the first system of coördinates, and at and near the second configuration will coincide with the third system of coördinates. This will give $D_1' = D_3''$. Again we may imagine a system of coördinates which at and near the first configuration will coincide with the second system of coördinates, and at and near the

* If we regard a phase as represented by a point in space of $2n$ dimensions, the changes which take place in the course of time in our ensemble of systems will be represented by a current in such space. This current will be steady so long as the external coördinates are not varied. In any case the current will satisfy a law which in its various expressions is analogous to the hydrodynamic law which may be expressed by the phrases *conservation of volumes* or *conservation of density about a moving point*, or by the equation

$$\frac{d\dot{x}}{dx} + \frac{d\dot{y}}{dy} + \frac{d\dot{z}}{dz} = 0.$$

The analogue in statistical mechanics of this equation, viz.,

$$\frac{d\dot{p}_1}{dp_1} + \frac{d\dot{q}_1}{dq_1} + \frac{d\dot{p}_2}{dp_2} + \frac{d\dot{q}_2}{dq_2} + \text{etc.} = 0,$$

may be derived directly from equations (3) or (6), and may suggest such theorems as have been enunciated, if indeed it is not regarded as making them intuitively evident. The somewhat lengthy demonstrations given above will at least serve to give precision to the notions involved, and familiarity with their use.