

Physics. — "*Statistical Electro-mechanics.*" By Dr. J. D. VAN DER WAALS Jr. (Communicated by Prof. VAN DER WAALS).

Prof. GIBBS has newly published a treatise entitled "Elementary principles in statistical mechanics", in which he communicates some considerations, belonging to a science, which he calls "Statistical mechanics," and of which he states that "on account of the elegance and simplicity of its principles" it is eminently worthy that the laws to which it is subjected, are studied. The laws relate to the behaviour of a great number of systems, whose motions are mutually independent. These systems quite agree with one another as to their nature, and only differ in so far, that the integration constants of the differential equations of motion have different values, or, what comes to the same, that the values of the generalized coördinates and of the generalized velocities at an arbitrary moment (e. g. at the moment $t = 0$) differ for different systems. The laws, which hold for such ensembles of systems have a very general character, as GIBBS shows; yet in their application they are confined to systems, consisting exclusively of ordinary matter. Now the question arises whether such like considerations might be applied to electro-magnetic systems, and whether in doing so we might extend our very limited knowledge of the phenomena of radiation in connection with the laws of thermodynamics.

We cannot deny however that we must not expect *too much* from these considerations. The greater part of the theses deduced by GIBBS are exclusively or principally applicable to ensembles of systems which he calls canonical and which have such an important place in his considerations, because they represent the simplest law possible of the distribution of the systems over the different "phases"¹⁾. Mathematical simplicity, however, is not a trustworthy criterion, when we want to investigate, what is actually to be found in nature. For our mathematical representation e. g. the simplest motion, a vibrating string can perform, is an harmonic motion, yet we should be utterly-mistaken if we should assume, that every vibrating string would execute such a motion. Perhaps we run the risk of making similar mistakes if we assume, that all systems in nature will follow the laws which we have deduced on the supposition of a canonical distribution of the systems of an ensemble.

It is true that GIBBS shows in his chapters XI—XIII that the cano-

¹⁾ Two systems are considered to be in the same phase when they are to be found in the same element of extension in phase.

neal distribution is the most probable one, provided the only condition, to which the ensemble is subjected, be that the mean value of the energy of the systems is a prescribed quantity; but the main difficulty happens to be to answer the question whether this is indeed the only condition. Systems e.g., consisting of spherical, mutually equal molecules, will not be distributed canonically, for they are still subjected to another condition, namely the distance of two centres of molecules can never be less than the diameter. To assume the canonical distribution comes therefore to the same as to neglect the volume of the molecules, but it is not easy to decide whether nothing else is neglected. In fact choosing the distribution of the systems of an ensemble is equivalent to choosing the cases, which we are to consider as "cases of equal probability" in a more direct application of the calculus of probabilities. Both are subject to the chance, that the probability a posteriori will prove to be another than we had assumed a priori.

Yet such like considerations can be useful, in the *known* region of thermodynamics, because they bring its laws very simply and elegantly together under one point of view; in the yet *unknown* region, because they may perhaps suggest formulæ, for which comparison with the experiments may decide, whether they are in accordance with the phenomena of nature or not.

Law of conservation of density-in-phase.

In an investigation, whether the considerations of GIBBS are also applicable for electro-magnetic systems, we have in the first place to examine, whether the "law of conservation of density-in-phase" holds also for them. In the beginning we will confine ourselves to systems devoid of material, electrical or magnetical masses.

Now we imagine an ensemble of systems. The different systems are congruent spaces, enclosed by perfectly reflecting walls. We divide each system into n equal cubic elements of space $dx\ dy\ dz$. These elements are so small that the electric and magnetic forces in them may be considered to be constant. The state of each system will be perfectly defined, if in each element of space the components f , g and h of the electric displacement, and the components α , β and γ of the magnetic induction are given. So the state is determined by means of $6n$ data; according to the assumption, that electric energy is potential, magnetic energy kinetic, the $3n$ components of the electric displacement would represent coordinates, the $3n$ components of magnetic conduction generalized momenta, or at least they would be proportional to them.

We mark the elements of space with successive numbers and represent the components of the vectors in the r^{th} element by $f_r, g_r, h_r, a_r, \beta_r$ and γ_r . Let us select from an ensemble those systems whose data lie between the limits f_1 and $f_1 + df_1, f_2$ and $f_2 + df_2 \dots f_n$ and $f_n + df_n$ and in the same way for the other components; the number of these systems may be represented by:

$$D df_1 \dots df_n dg_1 \dots dg_n dh_1 \dots dh_n da_1 \dots da_n d\beta_1 \dots d\beta_n d\gamma_1 \dots d\gamma_n$$

or
$$D [(df_1)] [(da_1)] \dots \dots \dots (1)$$

Here the brackets indicate, that also the other components, the parentheses that the same quantities also for the other elements of space are to be taken. We will call $[(df_1)] [(da_1)]$ an element of extension-in-phase, D the density-in-phase, $P = \frac{D}{N}$ the coefficient of probability-in-phase (N representing the total number of systems in the ensemble) and η , defined by the equation $P = e^\eta$, the index of probability-in-phase.

Let us consider the same ensemble after a short lapse of time dt , then the number of systems being in a certain phase, will have varied. We may conceive the variation of that number to be composed of $12n$ parts, as the systems may enter or leave a certain phase by passing one of $12n$ different limits, $[(f_1)], [(f_1 + df_1)], [(a_1)]$ and $[(a_1 + da_1)]$.

The systems passing the limit f_1 contribute:

$$D \frac{df_1}{dt} dt df_2 \dots df_n dg_1 \dots dg_n dh_1 \dots dh_n [(da_1)] \dots \dots \dots (2)$$

to the total number with which the quantity $D [(df_1)] [(da_1)]$ increases.

The systems passing the limit $f_1 + df_1$ contribute a decrease amounting to:

$$\left\{ D \frac{df_1}{dt} + \frac{\partial}{\partial f_1} \left\{ D \frac{df_1}{dt} \right\} df_1 \right\} dt df_2 \dots dh_n [(da_1)] \dots \dots \dots (3)$$

Adding these quantities we get an increase with:

$$- \frac{\partial}{\partial f_1} \left\{ D \frac{df_1}{dt} \right\} dt [(df_1)] [(da_1)] \dots \dots \dots (4)$$

Now we have:

$$\frac{\partial}{\partial f_1} \left\{ D \frac{df_1}{dt} \right\} = \frac{\partial D}{\partial f_1} \frac{df_1}{dt} + D \frac{\partial}{\partial f_1} \frac{df_1}{dt} \dots \dots \dots (5)$$

The second term of the second member is zero, for $\frac{df_1}{dt}$ depends only on the rotation of the magnetic induction, and is independent of the value of f_1 .

In the same way we find the increase in consequence of the systems passing the other limits, — taking into account that all quantities of the form $\frac{\partial}{\partial \alpha_1} \frac{d\alpha_1}{dt}$ are zero. — Taking the sum of all these partial increases and dividing by $[(d f'_1)] [(d \alpha_1)]$ we find :

$$\frac{\partial D}{\partial t} = - \left[\left(\frac{\partial D}{\partial f'_1} \frac{d f'_1}{dt} \right) \right] - \left[\left(\frac{\partial D}{\partial \alpha_1} \frac{d \alpha_1}{dt} \right) \right] \cdot \cdot \cdot \cdot \cdot \cdot (6)$$

or :

$$\frac{\partial D}{\partial t} + \left[\left(\frac{\partial D}{\partial f'_1} \frac{d f'_1}{dt} \right) \right] + \left[\left(\frac{\partial D}{\partial \alpha_1} \frac{d \alpha_1}{dt} \right) \right] = \frac{d D}{dt} = 0. \cdot \cdot \cdot (7)$$

Here $\frac{\partial D}{\partial t}$ represents the flucton of the density for a phasis whose limits are constant, $\frac{d D}{dt}$ for a phasis whose limits partake of the motion of the systems of the ensemble.

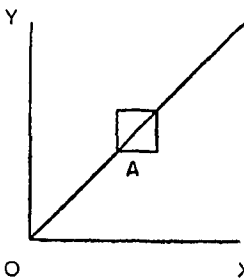
So the density proves to be constant for a phasis, partaking of the motion of the systems, and as, of course, the systems can never pass the limits of an extension-in-phase, when these limits move with the systems, the total number of systems within every extension-in-phase, i. e. $D [(d f'_1)] [(d \alpha_1)]$ remains constant, and so also $[(d f'_1)] [(d \alpha_1)]$.

This proof of the laws of conservation of density-in-phase and of extension-in-phase quite agrees with that one given by GIBBS. In our case, however, we have still to pay attention to one circumstance.

In calculating $\frac{\partial D}{\partial t} [(d f'_1)] [(d \alpha_1)]$, we have assumed, that this number is the sum of the numbers of systems passing the different limits. This comes to the same as to say that no system will pass more than one of the limits during the time dt , or at least, that the number of the systems that pass more than one limit is so small, that it may be neglected. In the proof of GIBBS we may assume, that this is really the case, provided we take dt so small, that $\frac{dq}{dt} dt$ is small

compared with dq (where q represents one of the generalized coordinates, and dq one of the dimensions of an element of extension-in-phase). For our case however this proof is incomplete. Be r and s two adjacent elements of space, then $[f'_r]$ and $[f'_s]$, $[\alpha_r]$ and $[\alpha_s]$ are no independent quantities, but they must be approximately equal, as $[f]$ and $[\alpha]$ vary only fluently from point to point.

In order to investigate the consequences of this circumstance we imagine an ensemble of



systems with only two coordinates x and y , which are subjected to the condition that x and y must be equal and continue to be so. All systems will then be found on the line OA and will move in the direction of this line, so all systems leaving the element of space drawn in the figure, or entering into it, will pass the two limits dx and dy at the same moment. If the condition is not that x and y must be rigorously equal, but only that their difference must be very small, then all systems will be huddled up very near the line OA and a great part of those that pass the limit dx will also pass the limit dy . It is evident, that this circumstance is caused by the fact, that within the element $dx dy$ the density is not homogeneous. If we choose therefore the dimensions dx and dy so small, that the whole element lies within a region, where the density may be considered as constant, then we may again assume that the number of systems, passing both limits may be neglected, compared with the number of systems passing only one of the two limits.

If we choose therefore $[(df_1)]$ and $[(d\alpha_1)]$ small compared with the mean value of $\left[\left(\frac{\partial f_1}{\partial x} dx\right)\right]$ and $\left[\left(\frac{\partial \alpha_1}{\partial x} dx\right)\right]$, so e. g. having a finite ratio to dx^2 , and dt again small compared with the quantities $[(df_1)]$ and $[(d\alpha_1)]$, so e. g. having a finite ratio to dx^3 , it appears that in fact the number of systems passing more than one of the limits may be neglected. So the proof of the law of conservation of density-in-phase is complete.

The quasi-canonical distribution.

If we wish to distribute the systems of an ensemble over the different phases in such a way, that the distribution does not vary with the time, so that the state of the ensemble is stationary, it is evident that we have to choose for P a function of the coordinates, which is constant in time. GIBBS chooses for this purpose the function

$e^{\frac{\psi - \varepsilon}{\theta}}$ where ε represents the energy of a system, and ψ and θ are constant quantities for a given ensemble. He calls this distribution the canonical distribution. This simple law cannot be applied to systems consisting of ether. If we assumed it, the quantities $[f]$ and $[\alpha]$ would vary abruptly from element to element instead of varying fluently, and moreover the distribution would depend on the dimensions of the elements of space, which we have arbitrarily chosen. We must therefore assume another distribution which secures a fluent variation of the electric and magnetic displacements.

To this purpose we will assume a distribution closely resembling those, discussed by GIBBS in his chapter IV as "other distributions having the same properties as the canonical." These distributions have the characteristic property, that the index of probability η is a linear function of one or more functions F_1, F_2 , etc. of the coordinates; the functions F_1, F_2 , etc. are subjected to the condition that their average value, taken over all systems of the ensemble must be a prescribed quantity. We might form different distributions, all satisfying the conditions. Now we seek the average value of η for all these different distributions; this average value of η will be a minimum for that ensemble where η is a linear function of F_1, F_2 , etc. This is proved by GIBBS in his chapter XI. I shall call such a distribution a quasi-canonical distribution. The canonical distribution is nothing else but such a quasi-canonical distribution where there is only one function F_1 and that represents the energy. As the canonical distribution is of little application, e.g. not for systems of molecules with finite diameter, it would perhaps have been preferable to give a broader meaning to the word canonical and to use it in the sense, in which I use quasi-canonical. As GIBBS has however used the word canonical exclusively for ensembles for which $\eta = \frac{\psi - \epsilon}{\theta}$, I will use the expression quasi-canonical for ensembles for which

$$\eta = \psi - aF_1 - bF_2 - \text{etc.}$$

In the ether we cannot have canonical ensembles, and so we will discuss only quasi-canonical ensembles. We put:

$$\eta = \frac{\psi - \epsilon}{\theta} - \frac{\varphi + \chi}{k} - \frac{\Omega_1 + \Omega_2}{\sigma_1} - \frac{\omega}{\sigma_2} \dots \dots \dots (8)$$

where, $d\tau$ representing an element of space:

$$\varphi = \int \left\{ \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right)^2 + \left(\frac{\partial h}{\partial x} - \frac{\partial f}{\partial z} \right)^2 + \left(\frac{\partial f}{\partial y} - \frac{\partial g}{\partial x} \right)^2 \right\} d\tau \dots \dots (9)$$

$$\chi = \frac{1}{16\pi^2 V^2} \int \left\{ \left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y} \right)^2 + \left(\frac{\partial \gamma}{\partial x} - \frac{\partial \alpha}{\partial z} \right)^2 + \left(\frac{\partial \alpha}{\partial y} - \frac{\partial \beta}{\partial x} \right)^2 \right\} d\tau \quad (10)$$

$$\Omega_e = \int \left(\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} \right)^2 d\tau \dots \dots \dots (11a)$$

$$\Omega_m = \int \left(\frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial y} + \frac{\partial \gamma}{\partial z} \right)^2 d\tau \dots \dots \dots (11b)$$

$$\omega = \frac{1}{\lambda} \int (f^2 + g^2 + h^2) \lambda d\sigma \dots \dots \dots (12)$$

k, σ_1 and σ_2 are constants, and σ_1 and σ_2 are infinitely small. The term $-\frac{\Omega_1 + \Omega_2}{\sigma_1}$ has been added, that we should have only to

deal with systems, consisting of free ether. Systems, containing electric masses are not absolutely excluded, but still their number is very small and may be neglected compared with that of the systems which are devoid of these masses. As $\frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial x} + \frac{\partial \lambda}{\partial y}$ is always zero, systems for which this expression has another value can never occur; yet we may admit them in such a small number, that they have no influence on the results. Finally we cannot take into consideration systems consisting of infinite space, for a finite quantity of energy would spread in it and we could not have a stationary distribution in the ensemble. Therefore it is necessary to enclose the electromagnetic energy within absolutely reflecting walls. But then it is necessary to add a term to η , which expresses, that the walls reflect absolutely, i. e. the quantities $[f]$ are always zero at the walls. The term $-\frac{\omega}{\sigma_2}$ expresses this; λ represents a small line in a direction normal to the surface; we make this line decrease indefinitely; $d\sigma$ represents an element of area.

If this distribution is to be for ether systems, what the canonical distribution is for material systems, then in the first place η must be a constant in time. For the other terms this is immediately evident, so we have only to show it for the term $\frac{\varphi + \chi}{k}$.

The relation, we have to prove may be written

$$\frac{d\varphi}{dt} + \frac{d\chi}{dt} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

We will make use of the relations

$$\frac{d\alpha}{dt} = 4\pi V^2 \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\frac{df}{dt} = -\frac{1}{4\pi} \left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and of the following relations, that may be deduced from them:

$$\frac{d^2 f}{dt^2} = V^2 \left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\frac{d^2 \alpha}{dt^2} = V^2 \left(\frac{\partial^2 \alpha}{\partial x^2} + \frac{\partial^2 \alpha}{\partial y^2} + \frac{\partial^2 \alpha}{\partial z^2} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and also of the corresponding relations for the other components. Now we have:

$$\frac{d\varphi}{dt} = \int \left[\left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right) \frac{d}{dt} \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right) \right] d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Integrating partially we get :

$$\frac{d\varphi}{dt} = \text{a number of surface integrals} -$$

$$- \int \left\{ \frac{df}{dt} \left(\frac{\partial^2 f}{\partial z^2} + \frac{\partial^2 f}{\partial y^2} - \frac{\partial^2 h}{\partial x \partial z} - \frac{\partial^2 g}{\partial x \partial y} \right) + \frac{dg}{dt} \left(\frac{\partial^2 g}{\partial z^2} + \frac{\partial^2 g}{\partial x^2} - \frac{\partial^2 f}{\partial x \partial y} - \frac{\partial^2 h}{\partial y \partial z} \right) \right. \\ \left. + \frac{dh}{dt} \left(\frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial x^2} - \frac{\partial^2 f}{\partial x \partial z} - \frac{\partial^2 g}{\partial y \partial z} \right) \right\} dt. \quad \dots \dots \dots (19)$$

In the coefficient of $\frac{df}{dt}$ in the cubic-integral we have :

$$- \frac{\partial^2 h}{\partial x \partial z} - \frac{\partial^2 g}{\partial x \partial y} = - \frac{\partial}{\partial x} \left(\frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} \right) = \frac{\partial^2 f}{\partial x^2} \quad \dots \dots (20)$$

at least if we put, $\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = 0$, so if we neglect the systems in which electric masses occur. So we get for the coefficient of $\frac{df}{dt}$ the expression $\frac{1}{V^2} \frac{\partial^2 f}{\partial t^2}$ and for the cubic integral :

$$- \frac{1}{V^2} \int \left[\frac{df}{dt} \frac{d^2 f}{dt^2} \right] d\tau = - \frac{1}{16\pi^2 V^2} \int \left[\left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y} \right) \frac{d}{dt} \left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y} \right) \right] d\tau = - \frac{d\chi}{dt}.$$

As at the absolutely reflecting walls $[f]$ and therefore also $\left[\frac{df}{dt} \right]$ continue to be zero, the surface integrals disappear; so equation (13) is proved.

The quantities φ and χ which are introduced in order that the variation of the electric displacement and the magnetic induction may take place fluently, are defined as the sum of the squares of the components of the rotations of those vectors, if we disregard the coefficient $\frac{1}{16\pi^2 V^2}$ introduced in order that equation (13) may be satisfied.

This seems to me the simplest definition for φ and χ . It might, however, appear that we are not yet sure that $\frac{\partial f}{\partial x}$, $\frac{\partial g}{\partial y}$ and $\frac{\partial h}{\partial z}$ get convenient values. In order to show that this is not the case, we will prove the following relations

$$\varphi = \int \left[\left(\frac{\partial f}{\partial x} \right)^2 + \left(\frac{\partial f}{\partial y} \right)^2 + \left(\frac{\partial f}{\partial z} \right)^2 \right] d\tau \quad \dots (21)$$

$$\chi = \frac{1}{16\pi^2 V^2} \int \left[\left(\frac{\partial \alpha}{\partial x} \right)^2 + \left(\frac{\partial \alpha}{\partial y} \right)^2 + \left(\frac{\partial \alpha}{\partial z} \right)^2 \right] d\tau \quad \dots (22)$$

where again the brackets indicate that we have to take also the cor-

responding terms in which the other components occur, In order to show this we expand the squares of equation (9) and consider separately the terms:

$$S = - \int \left\{ 2 \frac{\partial g}{\partial z} \frac{\partial h}{\partial y} + 2 \frac{\partial h}{\partial x} \frac{\partial f}{\partial z} + 2 \frac{\partial f}{\partial y} \frac{\partial g}{\partial x} \right\} d\tau \quad (23)$$

For $2 \frac{\partial g}{\partial z} \frac{\partial h}{\partial y}$ we write $\frac{\partial g}{\partial z} \frac{\partial h}{\partial y} + \frac{\partial y}{\partial z} \frac{\partial h}{\partial y}$ and integrate the first term partially according to z , the second according to y . The surface integrals vanish again and we get:

$$S = + \int \left\{ g \frac{\partial^2 h}{\partial y \partial z} + h \frac{\partial^2 g}{\partial y \partial z} + h \frac{\partial^2 f}{\partial x \partial z} + f \frac{\partial^2 h}{\partial x \partial z} + f \frac{\partial^2 g}{\partial x \partial y} + g \frac{\partial^2 f}{\partial x \partial y} \right\} d\tau$$

$$S = \int \left\{ f \frac{\partial}{\partial x} \left(\frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} \right) + g \frac{\partial}{\partial y} \left(\frac{\partial h}{\partial z} + \frac{\partial f}{\partial x} \right) + h \left(\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} \right) \right\} d\tau \quad (24)$$

$$S = - \int \left[f \frac{\partial^2 f}{\partial x^2} \right] d\tau \quad (25)$$

By integrating once more partially, where once more the surface integrals vanish, we get:

$$S = \int \left[\left(\frac{\partial f}{\partial x} \right)^2 \right] d\tau$$

so equation (21) is proved. Equation (22) is proved in the same way.

Three constants occur in the exponent η namely ψ , θ and k . ψ is a constant which must be chosen such, that integration of P over all systems of the ensemble yields 1. The two constants θ and k determine therefore the state of the systems. This is connected with the fact, that the nature of the radiation inside a closed surface, as LORENTZ¹⁾ has shown, depends besides on the temperature, also on the charge of the electrons by which the radiation is emitted. The fact that inside all bodies radiation of the same nature is formed, proves that in all bodies the electrons have the same charge. The constant quantity k must depend on that charge; it will therefore have the same value for spaces enclosed within all bodies as they are found in nature at least if the temperature is the same and its value would for a certain temperature only be different, if we imagined walls with electrons whose charge was different from those actually occurring.

¹⁾ LORENTZ. Proceedings. Vol. III, p. 436.