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Physics. — “*Some remarks on the mechanical foundation of thermodynamics.*”¹⁾ II. By Dr. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ.

(Communicated in the meeting of Januari 28, 1911).

§ 4. In § 2 I have discussed some ensembles and I have shown that they can be used to deduce the properties of a real system because they are connected with the time ensemble and because the majority of their systems is equivalent. I shall give in this paragraph another deduction which for this purpose may show the importance of the energy-space ensemble (and of the microcanonical one).

If in reality we want to obtain a system with a given energy we take a system of the same kind and supply energy to it or abduce energy from it, giving at the same time the appropriate values to the external coordinates. Let us suppose that it is possible for us to construct a system that contains exactly the required energy. If we do not take special care to get a system of a definite internal state, we shall obtain by our operations one of the systems possible with the given energy, but it will be impossible to indicate what kind of system will be produced. We can by no means practically regulate the internal state arbitrarily, as it is impossible for us to influence directly a single degree of freedom (e.g. the phase of the molecules). But we can only give the values we desire to the energy, density, or concentration in rather large parts, and even this with a moderate precision. If in a great number of cases we give the energy ϵ to a system we shall obtain it over and over again in other states, and the same will be the case if we bring the energy of a great number of systems together to the value ϵ .) The ensemble obtained in this way may be called a “real” energy space-ensemble.

Instead of giving the energy ϵ to N systems we can also select them in nature. I shall term the ensemble thus obtained a nature energy-space ensemble. The real and the nature energy-space ensemble

¹⁾ See These Proceedings page 817. Putting for the probability of the homogeneous system w_0 we find for that of a system specified by the numbers τ_r

$$w = w_0 e^{-\frac{n}{k} \sum_1^k \tau_r^2 \beta}$$

β is a function of the volume, the diameter of the molecules and the temperature.

²⁾ The circumstance must be taken into account that the original system will differ also in phase.

are not identical; the following considerations *mutatis mutandis* may, however, be applied to both. I shall therefore in the following pages only take into account the real energy-space ensemble. Constructing several times a real energy space ensemble, we shall find that the number of systems lying in a given element of the space E_{2n-1} , can differ in those cases. How great this number will be, cannot be said, if one does not know anything about the way in which the energy is supplied to the systems. If, however, we proceed without any scheme, the distribution of systems over the space E_{2n-1} will differ very little in the majority of possible cases. The distribution occurring in the majority of the possible cases must be stationary. The most simple stationary ensemble is the energy space ensemble discussed in § 2. ¹⁾

I shall now introduce the hypothesis that the real ensemble is identical with an energy space ensemble.

If we had supposed the energy of the considered systems to have a value between ε and $\varepsilon + d\varepsilon$, we should have found another kind of real ensembles which we can indicate by the term of real microcanonical ensembles. The most frequently occurring and stationary ensemble is the ensemble with a homogeneous distribution. (Comp. GIBBS Chap. XI and XII). ¹⁾

The introduced hypothesis enables us to deduce the properties of a real system with the help of the corresponding mean value in the energy space or the microcanonical ensemble. An arbitrary system can be obtained by choosing a system from a real ensemble; this real ensemble is an energy-space or microcanonical ensemble; the

¹⁾ The ensembles having the constant A different for the strips are also stationary. These must be taken into account if we know something more concerning the constants of integration.

²⁾ The distribution of systems in a real ensemble can be changed by the motion of the representing points, if it is not identical with the energy space-ensemble. It is impossible that in consequence of this motion an arbitrary real ensemble changes to an energy space ensemble, if the distribution for the strips of § 3 deviates from that in the energy space ensemble. Suchlike ensembles are, however, very rare among all the ensembles, built up of a given number of systems in the space E_{2n-1} . If the distribution over the strips agrees with that in an energy space ensemble, but is different from this inside the strips themselves, the ensemble will, by the motion of the systems, take states in which it deviates very little from an energy space ensemble but periodically it will again differ more from it. Also this kind of deviating ensembles is very rare. As for a real microcanonical ensemble, which shows a distribution different from the homogeneous, the distribution will differ after a long time as little as we like from the homogeneous in fixed elements of the space E_{2n-1} which are not too small. (Comp. GIBBS Chap. XII.)

properties of a real system are therefore those of a system chosen arbitrarily from one of those ensembles.

If we know that the state of a system is stationary, the properties of the system will agree with those of the most frequently occurring system of the ensemble; after a sufficiently long time every system will come to this state just for the very reason one would say that it can be thought to belong to a real ensemble. The idea of probability of a real system, which strictly speaking has only sense in relation to systems lying on the same path, can now be extended in the following manner: the system is produced by a construction which when repeated many times will lead to a real ensemble, the latter is identified with an energy-space (or microcanonical) ensemble; the probability that a real system is in a given state is therefore equal to the probability of the same state in the energy space or microcanonical ensemble¹⁾.

§ 5. In the following I shall consider the canonical ensembles. It is generally affirmed that these ensembles have no physical meaning and that their introduction is only justified because of the simplifications, which they allow when used in the calculations; also HERTZ adheres to this opinion²⁾. I think, however, that by changing a little the considerations which enabled us to ascribe a physical meaning to the microcanonical ensemble, i. e. by relating them to the real ensembles, we can attribute *in the same sense* a physical meaning to the canonical ensembles. If we know that in nature by the action of exactly determined causes a system of precisely the energy ε_0 would be formed, it is obvious to presume that in consequence of the small

¹⁾ By the following considerations we can avoid the mentioned hypothesis. Suppose that a real ensemble has been constructed \mathfrak{N} times; in each construction we take N times a point at haphazard in the space E_{2n-1} and unite the chosen points to an ensemble (or we proceed in the same way for the layer between ε and $\varepsilon + d\varepsilon$). Each possible real ensemble appears a certain number of times among the \mathfrak{N} ensembles constructed. The probability W of a given ensemble can be defined, as this number divided by the total number of ensembles \mathfrak{N} . If w represents

the probability of a given state in the ensemble under consideration then $\sum_1^{\mathfrak{N}} w_i W_i$ can be taken as the definition of the probability of a phase, the sum has to be extended over all the \mathfrak{N} ensembles. The hypotheses mentioned above means that we put the probability for the energy-space ensemble equal to 1 and take for w the probability in their ensemble.

²⁾ This simplification is often not so very important; most questions which can be solved by means of the canonical ensembles can be treated in a like manner without much complication, also by means of the micro-canonical ensembles.

and accidental deviations in the several causes not a system of exactly the energy ϵ_0 will be produced, but one of the energy ϵ ; in general $(\epsilon_0 - \epsilon)$ will be small in comparison to ϵ_0 . Positive as well as negative deviations will occur.

If we now construct a real system by trying to give the energy ϵ_0 to N systems or by choosing N systems of this kind in nature, we shall suppose that the probability that a system of the energy $\epsilon_0 + \epsilon'$ will be chosen is as great as that for the one with the energy $\epsilon_0 - \epsilon'$; a hypothesis which will be plausible as long as ϵ' is small. If the hypothesis is right, it may easily be shown that the canonical ensemble will play a part in the definition of the probability of a system.

In analogy of other cases (e. g. the law of errors) it seems admissible to suppose that in a real ensemble the number of systems whose energy lays between ϵ and $\epsilon + d\epsilon$ can be represented by

$$N \Delta e^{-(\epsilon - \epsilon_0)^2 / k} d\epsilon \dots \dots \dots (15)$$

It is not possible to prove this formula as long as we know nothing about the way in which the energy is supplied to the systems, or in which the energy ϵ_0 of the systems chosen from nature is determined ¹⁾.

If we form hypotheses on this subject we can deduce (15), but much importance should not be ascribed to such a deduction. ²⁾

Proceeding further in the same way as in the case of the micro-canonical ensembles we find for systems in the real ensemble which are represented in each layer between ϵ and $\epsilon + d\epsilon$ a homogeneous distribution.

¹⁾ If we suppose that the ensemble is constructed by choosing the systems from nature, the measurement of energy will be subjected to an error, the analogy with the law of errors therefore is still more obvious. Only we have now the difficulty that we do not know in what distribution the different systems of a certain energy appear in nature.

²⁾ To give an example take the following case. From a recipient of infinite energy, the energy is supplied to N systems. Equal portions z are supplied to a total amount of Nn portions to the systems of an initial energy 0. The supply of energy takes place in Nn distributions. In every distribution one system is taken from the N systems, the energy z supplied to it, and the system replaced among the others. This is Nn times repeated. It is evident that in a definite case not each system has obtained the energy $nz = \epsilon_0$, but it is possible to indicate the number of the systems containing an energy between $n'z$ and $(n'-1)z$. If the mentioned process is repeated several times, one distribution will be the most probable or most (frequently occurring) among all the possible distributions and this will be that for which (15) expresses the number of systems obtaining an energy between ϵ and $\epsilon + d\epsilon$. If z is infinitely small, we can be sure that the real ensemble obtained will be the ensemble characterised by (15).

If we represent the volume of the layer between $E_{2n-1}(\epsilon)$ and $E_{2n}(\epsilon + d\epsilon)$ by $e^{\varphi(\epsilon)} d\epsilon$, $\varphi(\epsilon)$ being a determined function of ϵ and we imagine an ensemble in which the density in the mentioned layer amounts to $f(\epsilon)$, this ensemble will be identical with the real ensemble if

$$\frac{f(\epsilon) e^{\varphi(\epsilon)}}{f(\epsilon_0) e^{\varphi(\epsilon_0)}} = e^{-\lambda(\epsilon - \epsilon_0)} \dots \dots \dots (16)$$

From (16) results

$$\log f(\epsilon) - \log f(\epsilon_0) + \varphi(\epsilon) - \varphi(\epsilon_0) = -k(\epsilon - \epsilon_0)^2$$

developing for small values of $(\epsilon - \epsilon_0)$ we get

$$\begin{aligned} (\epsilon - \epsilon_0) \left\{ \left(\frac{d \log f(\epsilon)}{d\epsilon} \right)_{\epsilon=\epsilon_0} + \left(\frac{d\varphi(\epsilon)}{d\epsilon} \right)_{\epsilon=\epsilon_0} \right\} + \\ + \frac{1}{2} (\epsilon - \epsilon_0)^2 \left\{ \left(\frac{d^2 \log f(\epsilon)}{d\epsilon^2} \right)_{\epsilon=\epsilon_0} + \left(\frac{d^2 \varphi(\epsilon)}{d\epsilon^2} \right)_{\epsilon=\epsilon_0} \right\} = -\lambda(\epsilon - \epsilon_0)^2. \end{aligned}$$

Therefore

$$\left(\frac{d \log f(\epsilon)}{d\epsilon} \right)_{\epsilon=\epsilon_0} = - \left(\frac{d\varphi(\epsilon)}{d\epsilon} \right)_{\epsilon=\epsilon_0}$$

and

$$\left(\frac{d^2 \log f(\epsilon)}{d\epsilon^2} \right)_{\epsilon=\epsilon_0} = - \left(\frac{d^2 \varphi(\epsilon)}{d\epsilon^2} \right)_{\epsilon=\epsilon_0} - 2k.$$

In first approximation

$$f(\epsilon) = f(\epsilon_0) e^{-\left(\frac{d\varphi(\epsilon)}{d\epsilon} \right)_{\epsilon=\epsilon_0} (\epsilon - \epsilon_0)} \dots \dots \dots (17)$$

If we suppose that this formula is true for all values of ϵ and that therefore $\frac{d^2 \log f(\epsilon)}{d\epsilon^2}$ can be put 0, we find for the number of systems having the energy between ϵ and $\epsilon + d\epsilon$

$$f(\epsilon_0) e^{\left(\frac{d\varphi(\epsilon)}{d\epsilon} \right)_{\epsilon=\epsilon_0} (\epsilon - \epsilon_0)} d\epsilon.$$

Putting $\left(\frac{d\varphi(\epsilon)}{d\epsilon} \right)_{\epsilon=\epsilon_0} = \frac{1}{\Theta}$ and $f(\epsilon_0) e^{\left(\frac{d\varphi(\epsilon)}{d\epsilon} \right)_{\epsilon=\epsilon_0} (\epsilon - \epsilon_0)} = N e^{\frac{\Psi}{\Theta}}$ we find for this number.

$$N e^{\frac{\Psi - \epsilon}{\Theta} + \varphi(\epsilon)} d\epsilon \dots \dots \dots (18)$$

so the ensemble is canonical. The relation to be adopted between k and

$\left(\frac{d^2 \rho(\epsilon)}{d\epsilon^2}\right)_{\epsilon=\epsilon_0}$ does not follow as far as I can see from the physical signification of these quantities ¹⁾.

GIBBS has proved that the quantity $\left(\frac{\partial \mu(\epsilon)}{\partial \epsilon}\right)_{\epsilon=\epsilon_0}^{-1}$ has properties corresponding with those of temperature. The mentioned quantity, however, has a definite value for a given value of the energy ϵ_0 , so the modulus of the canonical ensemble used has to be put equal to the value of $\left(\frac{\partial \rho}{\partial \epsilon}\right)_{\epsilon=\epsilon_0}^{-1}$. The ensemble defined by (15) and the canonical ensemble (18) deviate slightly from each other, but these deviations are of less significance the greater the number of degrees of freedom is. The deviations are most important for those systems of which the energy ϵ is such that $(\epsilon-\epsilon_0)$ is large in comparison to ϵ_0 , but suchlike systems are very infrequent in both ensembles. We can without fearing errors in our results suppose the real ensemble to be a canonical one, and if we further suppose that in the real ensemble the distribution in every layer is homogeneous, we find for the probability of a system in the real ensemble

$$e^{-\frac{\Psi-\epsilon}{\Theta}} dp_1 \dots dq_n \dots \dots \dots (19)$$

The identity of the real and the canonical ensemble is no more fully proved or to be proved completely than that of the micro-canonical or energy-space ensemble. It exists in this respect that the number of systems in the layer $\epsilon \dots \epsilon + d\epsilon$ can be represented by $f(\epsilon)d\epsilon$, $f(\epsilon)$ being a maximum for $\epsilon = \epsilon_0$, as well for the real as for the canonical ensembles; in the microcanonical ensembles without it $f(\epsilon) = 0$, to a certain degree the latter ensembles have therefore less physical sense than the canonical, provided that we do not take as startingpoint the single system and with it the time-ensemble, but take into account that a given system has a not totally definite energy.

§ 6. HERTZ has developed in the paper mentioned considerations about the theorem that two systems of equal temperature produce

¹⁾ GIBBS has proved (Chap IX (350)) that we have the relation

$$-\left(\frac{d^2 \rho}{d\epsilon^2}\right)_{\epsilon=\epsilon_0} = \frac{1}{(\epsilon-\epsilon_0)^2}$$

In the real ensemble (15) the mean value $\overline{(\epsilon-\epsilon_0)^2}$ is equal to $2k$, therefore in the real and the canonical ensemble the mean value of the squares of deviations are equal

after their union a system of the same temperature. He supposes the connection performed in such a way that the two systems form together a new system, of which the reciprocal energy is small in comparison with $\varepsilon_1 + \varepsilon_2$. The connection enables the systems to interchange energy. The quantity τ of HERTZ is related to the average kinetical energy in the ensemble and is interpreted by:

$$\overline{\varepsilon_p} = \frac{n}{2} \frac{V}{\omega} = \frac{n}{2} \tau,$$

n being the number of degrees of freedom, V the volume of the extension in phase where the energy of the represented systems is less than ε , ω is put instead of $\frac{\delta V}{\delta \varepsilon}$.

HERTZ determines in a very elegant manner the conditions necessary for two microcanonical ensembles of the energies ε_1 and ε_2 and having $\tau_1(\varepsilon_1)$ equal to $\tau_2(\varepsilon_2)$ to form after their connection an ensemble of the energy $\varepsilon_1 + \varepsilon_2$ and the temperature $\tau_{12}(\varepsilon_1 + \varepsilon_2)$ so that

$$\tau_{12}(\varepsilon_1 + \varepsilon_2) = \tau_1(\varepsilon_1) = \tau_2(\varepsilon_2).$$

His considerations teach us only something about the equilibrium of temperature for stationary systems if we have shown that the average kinetical energy of a degree of freedom is equal to that in the most frequently occurring system, while the conditions of HERTZ are complied with. We shall suppose this as proved and if we then consider that two ensembles of energy ε_1 and ε_2 and of equal τ -value produce an ensemble of the same τ -value, and that the mean kinetical energy in the original ensembles is also equal and with it the kinetical energy of the most frequently occurring systems, we shall find that also the temperature of the stationary systems are equal before and after the union.

Even if we unite systems in non-stationary state, we can deduce something. If the temperature of the considered systems would be equal after they had come to a stationary state, they would belong to ensembles of equal τ . The system formed by their union belongs to an ensemble with the same value of τ , the temperature therefore adopted by the system formed if we unite two non-stationary systems is, if this system has become stationary the same as that which would have been adopted by the separate systems in their stationary state.

Also for the canonical ensemble we find the same results. GIBBS

¹⁾ Conf. P. HERTZ loc. cit. p. 243.

²⁾ For gases and fluids I have proved this in my dissertation.

has proved that the modulus Θ corresponds in all respects with the temperature. The mean value of kinetical energy in an ensemble is $\frac{n}{2} \Theta$ and this average value is equal to the corresponding value for most frequently occurring and stationary system, Θ can therefore be used to define the temperature of a stationary system.

Groningen, Dec. 1910.

Physics. — “On vapour-pressures in binary systems with partial miscibility of the liquids.” “VAN DER WAALS-fonds” researches N^o. 2. By Prof. P. H. KOHNSTAMM and Dr. J. TIMMERMANS. (Communicated by Prof. J. D. VAN DER WAALS).

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In these Proceedings Vol. 9—11 ¹⁾ VAN DER WAALS derived a series of conclusions concerning systems of not completely miscible liquids. In this communication we shall compare three of these conclusions with the experimental data which are to be found on this subject in the literature, and with the results of some new determinations, which follow here.

We shall discuss the three following points:

1. The shape of the p, T -projection of the three-phase curve $L_1 L_2 G$.
2. The connection between the shape of the plaitpointline and the existence of a maximum in the p, x -section of the surface of saturation.
3. The occurrence of points of inflection in the p, x -section of the surface of saturation specially in the neighbourhood of a critical end-point.

§ 1. VAN DER WAALS has tried to demonstrate that the p, T -projection of the three-phase line does not intersect the plaitpoint line in a critical end-point, but touches it. From this very remarkable results would follow.

a. In the case of splitting-up of the plaitpoint line the three-phase pressure would ascend regularly with rise of temperature. As, however, one of us ²⁾ remarked already before, $\frac{dp}{dT}$ has a very high value for this line in the case of splitting up of the plaitpoint line $\left(\frac{dT}{dp}$ never becomes higher than 0,04 degree per atmosphere); and so the three-

¹⁾ See also Archives Néerl. (2) XIII p. 249—288 (1908).

²⁾ J. TIMMERMANS. Handelingen van het 13e Vlaamsche Congres 1909 p. 120.