

Citation:

Waals Jr., J. D. van der, On the law of the partition of energy in electrical systems, in:
KNAW, Proceedings, 11, 1908-1909, Amsterdam, 1909, pp. 580-590

Physics. — “*On the law of the partition of energy in electrical systems.*” By Prof. J. D. VAN DER WAALS JR., (Communicated by Prof. J. D. VAN DER WAALS).

It is well known that MAXWELL was the first to pronounce the thesis that in the case of statistical equilibrium every degree of freedom will possess on an average the same amount of kinetic energy. In my opinion BOLTZMANN's and GIBBS's investigations have raised the validity of this thesis for the systems to which their theory applies, above doubt. And yet this result is difficult to reconcile with the experimental data. It has already long been known that the gas molecules must undoubtedly possess more degrees of freedom than would follow from the specific heat at constant volume in connection with this law.

BOLTZMANN ¹⁾, GIBBS ²⁾ and others have expressly stated that systems, as they occur in nature, always exhibit important points of difference with the systems for which the said law was proved. For BOLTZMANN and GIBBS have drawn up their statistical theory exclusively for systems which have a finite number of degrees of freedom, and for which the equations of classical mechanics hold. The systems occurring in nature, on the other hand, always contain electrical charges; so we have always to deal with the ether with its infinite number of degrees of freedom. Moreover for the changes of the coordinates no longer the mechanical laws are exclusively to be taken into consideration, but also the fundamental equations of the theory of electricity.

In view of this an extension of the statistical method, in such a way that it applied also to electrical phenomena, was urgently required. An attempt at such an extension was made by JEANS ³⁾ and by LORENTZ ⁴⁾. They arrived both at the conclusion that also in this case the law of equal partition of energy holds. Their considerations, however, pointed out a new difficulty. When every degree of freedom possesses the same amount of kinetic energy, the ether with its infinite number of degrees of freedom would finally acquire all the energy. A consequence of this would be that in case of equilibrium between a material system and the ether, as is found in all heat phenomena in consequence of the radiation, the velocities of the molecules and the electrons would become zero. Moreover the ether would then have to contain the energy in such a way that all the

¹⁾ L. BOLTZMANN, Wiener Sitzungsab. LXIII p. 418. a. 1871.

²⁾ J. W. GIBBS, Statistical Mechanics. p. 167.

³⁾ J. H. JEANS, Phil. Mag. Series VI. Vol. X, p. 91, 1905.

⁴⁾ H. A. LORENTZ, Nuovo Cimento, Series V. Vol. XVI.

energy had accumulated on the side of the infinitely small wave-lengths.

It is clear that here too theory is in direct contradiction with experience. Still it is easy to see that we must come to this conclusion if we assume the three following suppositions:

A. The relation $\sum_{i=1}^{i=n} \frac{d\rho_i}{dp_i} = 0$ is satisfied. Here n represents the

total number of independent variables, ρ_i an arbitrary of these variables. In mechanics both the generalized coordinates and their time variations or the corresponding momenta are to be considered as independent, so that in a mechanic system n represents twice the number of degrees of freedom.

B. There is statistical equilibrium.

C. All the phases (in the sense of GIBBS) representing the same energy, lie on the same path.

By JEANS¹⁾ and by W. RITZ²⁾ attempts have been made to explain this contradiction between theory and observation. In a certain sense also by M. PLANCK, though the latter does not start from GIBBS's statistical method in his theory of radiation. As none of these theories satisfies me entirely, I shall state here another direction in which a solution of the contradiction might be sought. Before proceeding to this, however, I consider it my duty to indicate why the three theories mentioned do not satisfy me, as else I should not be justified in adding another view to the number of existing ones.

On a superficial consideration RITZ's theory makes the impression to look for the solution of the difficulty in this that it rejects supposition C. For RITZ wants to reject a great number of states of the electromagnetic field which are compatible with the field equations, because in his opinion they cannot occur. Thus he assumes only waves originating from electrons, not such ones as converge on them, because, if the latter existed, the electron would be a perpetuum mobile. From these words it appears already that it is really supposition B that is rejected by RITZ. The system he considers, constantly loses energy, and so it is not in equilibrium. If we think the material universe to occupy a finite space surrounded by an ether which reaches to infinity, it must of course lose energy, and cannot be in equilibrium. But then we knew already that on account of the prevailing differences of temperature the material universe is not in equilibrium. We have always only to deal with limited systems which are surrounded by other systems, and which are only for a

¹⁾ Comp. i. a. l. c. and Phil. mag. Series VI. Vol. II, p. 638.

²⁾ Ritz. Phys. Zeitschr. Vol. IX. No. 25 p. 907. Anno 1908.

certain limited time excluded from external influence, and may be considered to be in equilibrium. During the time, however, that the equilibrium exists, every particle must on an average absorb as much energy as it emits. So an inward radiant vector must exist during that time.

But, says RITZ, when we consider a finite system, we must always think it enclosed within walls which contain a finite number of electrons, and which therefore can reflect the radiation in fewer ways than LORENTZ'S totally reflecting walls can. So LORENTZ'S theory is not applicable to the natural systems. This really offers a difficulty. Even the γ -rays of radium pass through metal screens in a considerable degree, and it is possible that vibrations of still smaller wave-length possess so great a penetrating power that they are never in equilibrium of radiation in our experiments. Yet it seems to me that there are facts which indicate that in RITZ'S observation, which is quite correct in itself, the clue to the explanation of the normal spectrum is not to be found. For it seems to me that if RITZ'S explanation was the true one, the spectral formula of RAYLEIGH would have to hold for all wave-lengths which are still regularly reflected by the walls, which is by no means the case. Moreover, we should then have to expect that this formula would be fulfilled with the greater degree of approximation as the walls were thicker, and so more wave-lengths were approximately in equilibrium of radiation; then we should not find a definite spectral formula independent of the thickness of the walls. We may finally imagine the walls to be infinitely thick, so that they would contain an infinite number of electrons, and RITZ has not shown that also in this case his restriction of the number of possibilities in the inward radiation originating from the walls, is justified.

While RITZ'S theory deals only with the normal spectrum, JEANS tries at the same time to find a solution of the difficulties attached to it, and of the difficulties attached to the specific heats. He, too, thinks that he has to find the solution in the fact that supposition *B* is not satisfied. He thinks, namely, that the coordinates of a system may be divided into two kinds: 1 those which we may call conservative coordinates, which possess an appreciable kinetic energy; 2 those which we may call dissipative coordinates, which can receive energy from the conservative ones only exceedingly slowly, and which lose the energy they have received so rapidly by radiation, that they never possess an appreciable quantity of energy. Then the kinetic energy which must be ascribed to systems agrees with their number of conservative coordinates and so is less than would cor-

respond with the total number of degrees of freedom. So this agrees with what we observe with regard to specific heat.

An objection to this theory is, that it is inexplicable how such a system could be heated by radiation. For then the dissipative coordinates would first absorb heat, and then transfer it to the conservative coordinates. But they can only transfer it, when on an average they have more kinetic energy than the conservative coordinates. So if such a body was exposed to the radiation of a hotter body, it would absorb very much heat before the temperature began to rise, and on further heating by radiation the dissipative coordinates, too, would have to receive energy, and the specific heat would therefore be greater than when the heating was done by conduction. On account of these and similar conclusions which might be made from JEANS'S theory, this theory did not seem satisfactory.

Finally in PLANCK'S theory it is not possible to ascertain which of the three suppositions is to be rejected. Still it is clear that we can never obtain PLANCK'S spectral formula, if we accept the three suppositions. His suppositions must, therefore, be incompatible with the three suppositions given here, and probably the hypothesis that the energy can only be absorbed in fixed energy-quanta, will be irreconcilable with our suppositions. Of course, this is no objection to PLANCK'S theory; the assumption of the three suppositions bringing us into conflict with experience, one of them must in reality not be fulfilled. Of more importance seems to me the objection that the supposition of these fixed quanta of energy which can only be absorbed or radiated as a whole, and which, moreover, have a different amount for radiation of different wave-length, clash altogether with all our ideas on the behaviour of vibrators, and that it is difficult to see how it could be reconciled to the ordinary laws of radiation by vibrators, of which PLANCK also made use in his theory.

Nor would this objection perhaps suffice to make us reject the theory, when there were urgent reasons why we should have to assume the existence of these energy-quanta. In my opinion, however, these urgent reasons are wanting. PLANCK used the supposition of the existence of these energy-quanta to bring two equations into harmony, which have been derived in an entirely different way. One¹⁾ has been derived from the laws of BOLTZMANN (STEPHAN) and WIEN, which are again derived from the 2nd law of thermodynamics in connection with the fundamental equations of the theory of electricity, and which, therefore, hold for all the systems for which these laws hold.

¹⁾ M. PLANCK. Vorlesungen über die Theorie der Wärmestrahlung p. 149 equation 223.

This equation runs $S = F\left(\frac{u}{\nu}\right)$, in which S represents the entropy, u the energy, ν the frequency of the free vibrations of the vibrator and F a still unknown function. The other equation¹⁾ may be written $S = F\left(\frac{u}{\varepsilon}\right)$ in which ε represents a small quantum of energy, into which the total energy of all vibrators with frequency ν is divided, after which these atoms of energy are distributed over the different vibrators according to the laws of probability. If these equations are to be in harmony, ε must really be $= h\nu$, as PLANCK assumes. The question, however, is, whether there is sufficient cause to assume that these equations do harmonise. And in my opinion this is not the case. For the first equation holds for real bodies, the second for the fictitious systems of vibrators, which most likely do not occur in the real bodies. In the first place so many different kinds of vibrators with so many different free periods are hardly to be assumed. And moreover every vibrator will, no doubt contain a moving electron whose motion strictly speaking is controlled not by a differential, but by an integral equation, so that the vibrator has not one, but a whole series of periods for its free vibrations.

Now PLANCK asserts that it is of no importance whether his radiating systems agree with those really occurring in nature. For, he says²⁾, KIRCHHOFF's law teaches that we always get the same normal spectrum independent of the nature of the walls. This, however, seems to me an inaccurate interpretation of the law of KIRCHHOFF. For this law states only something about walls occurring in nature, but it does not decide anything about the spectrum that would be formed in a space inclosed by walls with fictitious properties which deviate from what really occurs in nature. Hence the interpretation of KIRCHHOFF's law that the spectrum would be independent of the nature of the walls, is to be rejected. The real gist of the law is much better rendered by saying that all walls occurring in nature have such properties, that they give rise to the same spectrum; what these properties are which all real walls have in common, is not yet quite known. Only on special suppositions did LORENTZ³⁾ succeed in examining this.

That this acceptance of KIRCHHOFF's law is really the correct one appears from this that in his cited paper LORENTZ succeeded in imagining walls of such a nature that the thermodynamic laws of radiation are not fulfilled in their mutual radiation. He imagined,

¹⁾ loc. cit. p. 153 in the middle.

²⁾ loc. cit. p. 100 and 101.

³⁾ H. A. LORENTZ, These Proc. IX p. 436, 1900.

viz., two uniform systems, of which the linear measures of the second are α -times larger, all masses β -times larger, and all charges of corresponding parts β/α -times larger than of the first. It now appeared that when the velocities of the parts of the systems were the same, that then the ratio of the electrical forces in corresponding points was $\sqrt{\beta/\alpha^3}$, so the ratio of the densities of energy β/α^3 . Then, however, the ratio of the temperatures is as that of the kinetic energy of corresponding particles, i. e. $\beta:1$, so that the law of BOLZMANN is fulfilled only when $\beta^2 = \beta/\alpha^3$ or $\beta = 1/\alpha$. As, however, it is always possible to imagine these systems in such a way that α is not $1/\beta$, it appears that the thermodynamic laws of radiation are not fulfilled for arbitrarily chosen systems. So when we make arbitrary suppositions concerning the nature of the walls, we run a great risk of choosing them in such a way that the spectral distribution with which they would be in equilibrium, does not agree with the real normal spectrum, this could only be incidentally the case. And so there is no ground to assume that the two formulae of PLANCK mentioned represent the same spectrum, which removes the ground for the assumption of the energy-quanta.

JEANS¹⁾ considers it a difficulty to assume that walls could be imagined for which the thermodynamic laws of radiation are not fulfilled. I do not see the difficulty. The thermodynamic laws are only empiric laws. And when we come to the conclusion that the radiation of arbitrarily imagined walls does not satisfy the second law of thermodynamics, whereas experience teaches that the real radiation does satisfy it, we have simply to conclude from this that such walls do not occur in nature. We should, indeed, meet with a difficulty, if we could show that the laws of thermodynamics *had to* be applicable to all conceivable systems. The statistical derivation of these laws seems really to imply this. This, however, is only seemingly the case. For any fictitious system, whatever properties we ascribe to it, a state of statistical equilibrium will, no doubt, exist which is characterized by the fact that a certain quantity, which we may call the probability, is maximum. If we call the logarithm of the probability entropy, then for every system the theorem will hold that with given energy and volume this entropy is maximum. But it has not been proved a priori that the entropy defined in this way, is always represented by $\int \frac{dQ}{T}$, or at least it has only been proved for mechanical systems, and not for electrical ones,

¹⁾ J. H. JEANS, Phil. Mag. Series VI Vol. XII p. 57, 1906.

which we are now discussing. It is not even self-evident by any means that a temperature could be defined for every conceivable system. And we even know that two walls of the nature LORENTZ has loc. cit. imagined, when their particles had the same kinetic energy, so that they were in equilibrium of temperature as regards their conduction of heat, would transfer heat to each other by radiation. And reversely, they would not be in equilibrium of conduction of heat when they were in equilibrium for the radiation. As now in the derivation of the law of STEPHAN with the aid of the cycle of operations described by BARTOLI and BOLZMANN use is made of the supposition that $\eta = \int \frac{dQ}{T}$, this law need not hold for an arbitrarily imagined body, and can only do so incidentally.

In virtue of the above I think that other explanations are called for, which might be able to reconcile theory and observation. And it seems to me that such an explanation might be found in this direction that we assume that the supposition *A* is not fulfilled, and this we may do without introducing new hypotheses, without coming in conflict with the current theory of electricity. It is true that JEANS and LORENTZ have come to the conclusion that supposition *A* is satisfied, but it seems to me that their considerations only refer to electrons which possess a mechanical mass; they do not seem to apply to electrons without mechanical mass.

To show this we shall consider systems agreeing with those examined by LORENTZ¹⁾. A number of electrons are enclosed in a parallelepiped space with totally reflecting walls. It is true that the objection advanced by RITZ to such walls, is not to be entirely refuted, but without this supposition we can never imagine a system in statistical equilibrium, and when we think the space so large that the radiation reflected by the walls, has long been absorbed before it has reached the central parts, the condition in the central parts will most likely not be influenced by the walls. Besides, the reflected radiation will behave in almost the same way as if it was emitted by a medium of the same nature outside the enclosed space, so that also the parts lying nearer the walls will probably be in the same condition as if the walls did not exist, and the medium extended also outside the walls.

I shall assume the electrons to be spherical, so that their position is entirely determined by the cartesian coordinates *XYZ* of the centre. As further data I shall choose the electrical and the magnetical forces in the different elements of space. In their stead we might

¹⁾ H. A. LORENTZ, Nuovo Cimento I. c.

also have chosen the coordinates used by LORENTZ; this would have been more symmetrical and more elegant. The coordinates chosen by me however, may allow us to determine the quantities, which we wanted to determine, in a somewhat simpler manner. For the rest the result of the investigation is the same in the two cases.

It is, however, clear that we may not choose the three components of the electrical force \mathfrak{E} and the magnetic force \mathfrak{H} quite arbitrarily in every point. For \mathfrak{H} must satisfy the equation $\text{Div. } \mathfrak{H} = 0$, and $\text{Div. } \mathfrak{E}$ is also determined in every point if X , Y , and Z are given for every electron. So if we take \mathfrak{E}_x , \mathfrak{E}_y , \mathfrak{H}_x and \mathfrak{H}_y as independent variables, \mathfrak{E}_z and \mathfrak{H}_z are determined, with the exception of the constant of integration. This constant, however, is not arbitrary, but determined by the conditions that the normal component of \mathfrak{H} and the tangential one of \mathfrak{E} must be zero at the walls. These conditions yield more equations than the number of constants at our disposal. Hence we have still to diminish the number of independent variables by considering still fewer components as independent variables in the elements adjoining the wall. However, I do not think this will affect our further reasoning.

Of course the conditions $\text{Div } \mathfrak{E} = \rho$ and $\text{Div } \mathfrak{H} = 0$ cannot be rigorously satisfied, when we really think \mathfrak{E} and \mathfrak{H} constant within the elements. We can then take it e. g. in such a way that we understand the mean values in the elements by the given components of \mathfrak{E} and \mathfrak{H} , while inside these elements \mathfrak{E} and \mathfrak{H} are linear functions of x , y and z , and they do not show any discontinuities on the boundaries of the elements.

The changes of state in our systems are now determined by the following equations:

$$c \text{ Rot } \mathfrak{E} = - \frac{d\mathfrak{H}}{dt} \quad c \text{ Rot } \mathfrak{H} = \frac{d\mathfrak{E}}{dt} + \rho v$$

$$\int \rho (\mathfrak{E} + [v \cdot \mathfrak{H}]) dv = m \dot{v}_0$$

$$\int \rho [r (\mathfrak{E} + [v \cdot \mathfrak{H}])] dv = M \dot{w}$$

In these latter two vector formulae, which yield six scalar equations when written down for the different components, r represents the radius vector from the centre of the electron to an arbitrary point, m the mass, M the moment of inertia, and v the velocity of an arbitrary point, so that $v = v_0 - [r w]$, when v_0 denotes the velocity. If this value of v is substituted, six equations are obtained in which the six components of v_0 and w occur linearly.

We have here at once to distinguish two cases:

1. m and M are not zero, i. e. we assign a real mass to the

electrons. In this case the equations serve to determine the accelerations, the velocities are to be considered in this case as independent variables.

2. For some electrons m and M are zero. In this case the accelerations disappear from the equations. Now we can solve the components of v_0 and w in determinant form, as they form a set of six linear equations. The elements of this determinant are integrals which are to be extended over the electron, and are known if \mathfrak{E} and \mathfrak{H} have been given in every point. So v_0 and w appear not to be independent variables in this case. The number of variables is, therefore, smaller than in the case that the masses are not zero. And this is not strange: in the expression of the kinetic energy the velocities of the electron do not occur when we ascribe the energy to the medium. Only if by the supposition of a quasi-stationary motion a connection is established between the motion of the electron and the forces of the field, the equation of the energy can be reduced to such a form that v_0 and w occur in it.

The values of v_0 and w thus found must now be substituted in the equation $c \operatorname{Rot} \mathfrak{H} = \frac{d\mathfrak{E}}{dt} + \rho v$ to find the value of $\frac{d\mathfrak{E}}{dt}$.

If we now examine in how far supposition A has been fulfilled, it is at once evident that this is certainly the fact in the first case.

Then $\frac{\partial \dot{\rho}}{\partial p} = 0$ even for every variable separately.

In the second case, however, it is different, then $\frac{\partial v_0}{\partial X}$ is not zero.

For the integrations occurring in the elements of the determinant which determines v_0 , must be extended over another region when the electron is displaced. When differentiating we should bear in mind that \mathfrak{E}_z is determined from ρ , whereas ρ changes in the points of the space if the electron is displaced, so that \mathfrak{E}_z is to be considered as function of X, Y, Z .

It follows from $\frac{d\mathfrak{H}}{dt} = - \operatorname{Rot} \mathfrak{E}$ that $\frac{d\mathfrak{H}}{dt}$ is independent of \mathfrak{H} , so

that the terms $\frac{\partial \frac{d\mathfrak{H}}{dt}}{\partial \mathfrak{H}}$ are zero. The same holds for the terms $\frac{\partial \frac{d\mathfrak{E}_x}{dt}}{\partial \mathfrak{E}_x}$

for elements which fall outside the electrons; but not for terms inside them. For there $\frac{d\mathfrak{E}_x}{dt}$ is determined by $\frac{d\mathfrak{E}_x}{dt} = \operatorname{Rot}_x \mathfrak{H} - \rho v_x$ and v_x

being dependent on \mathfrak{E}_x , this is also the case for $\frac{d\mathfrak{E}_x}{dt}$. It is true that

$\frac{\partial}{\partial \mathfrak{E}_x} \frac{d\mathfrak{E}_x}{dt}$ becomes very small for every element, and zero in the limiting case that we take infinitesimal volume-elements, but the sum of these quantities for all the elements falling within a certain electron does not become zero, but when the volume-elements become infinitely small it verges to a certain limit, which is not to be neglected by the side of $\frac{\partial r_{vx}}{\partial X}$. Here too, we must remember that we must not only differentiate with respect to \mathfrak{E}_x where this quantity occurs explicitly, but also that \mathfrak{E}_z depends on \mathfrak{E}_x . For by varying \mathfrak{E}_x , we vary q , unless we take care to bring about a suitable modification in \mathfrak{E}_z in the surrounding elements.

Equation $\frac{1}{D} \frac{dD}{dt} = - \sum_{r=1}^n \frac{\partial j_r}{\partial p_r}$ now indicates that we have a stationary state if on every path covered by a system the density of phase

is made to satisfy $D = e^{-\frac{1}{\mathfrak{h}} \int \sum \frac{\partial j}{\partial p} dt}$. On account of the intricate form which $\sum \frac{\partial j}{\partial p}$ assumes it seems hardly possible to draw further conclusions, unless we succeed by a felicitous reduction or by making a better choice of the independent variables from the beginning in rendering this sum in a much simpler form.

For the present I must confine myself to pointing out that it seems that in this direction a solution is to be found of the contradiction which has existed up to now between theory and observation. And if this should prove to be the only way in which this can be done, it is a qualitative proof of the existence of electrons without mechanical mass.

We must, however, point out that it can only prove that some electrons do not possess any mechanical mass, not that this would have to be the case for all electrons. For as soon as electrons without mechanical mass occur, the relation $\sum \frac{\partial j}{\partial p} = 0$ is not fulfilled. The supposition that some, e. g. the positive electrons will possess mechanical mass, and others e. g. the negative electrons not, is by no means excluded by these considerations.

If we should take Kirchhoff's law as holding for arbitrarily imaginable walls, the partition of the energy in the normal spectrum would of course never enable us to conclude anything concerning the nature of the bodies by which the radiation is emitted. If, however,

this view is the correct one that the bodies give the same spectrum only because they have certain properties in common, then it must be possible to learn something about these properties from the partition of energy in the spectrum. And thus we may hope that a further development of the application of the statistical method to electrical systems may tend — not to find an accurate formula for the spectrum, which would only be possible if we a priori perfectly knew the nature of the electrons — but rather to test whether a hypothesis concerning the nature of the electrons gives rise to the correct spectral formula, and so whether it is to be accepted or rejected.

Botany. — “*Some remarks on *Sciaphila nana* Bl.*” By Prof. F. A. F. C. WENT.

While working at the *Triuridaceae*, collected by Mr. G. M. VERSTEEG during the expedition to Southern New-Guinea in 1907, I have also examined the plants of the same order, which are found in the Botanical Museum of the University of Utrecht. In so doing I came across alcoholic material of a *Sciaphila* brought from Buitenzorg by Mr. PULLE and collected at Tjiomas.

When an attempt was made to name this plant, it at once became evident, that it was not *Sciaphila tenella* BL. and it was therefore surmised that the other species described for Java, namely, *S. nana* BL., had been met with. Now the diagnosis of BLUME is of such a nature, that it is impossible with its aid to recognize the species¹⁾; nor are the figures of his plate XLVIII conspicuously clear. I soon found, by comparison with BECCARI's monograph of Malay *Triuridaceae*, that the specimen in question evidently agreed completely with his *S. corniculata*²⁾. I will shortly give detailed proof of this identity, but first remark that BECCARI himself had noticed the agreement between BLUME's *S. nana* and his own *S. corniculata*, for he speaks of *S. nana*³⁾ as follows:

“Non ho visto questa Specie, ma dalla figura lasciata da BLUME mi sembra poterla includere nel gruppo della *S. corniculata* e della *S. Arfakiana*”.

In order to obtain greater certainty I have examined the original specimen of BLUME's in 's Rijks Herbarium at Leiden.

Under the name of *Sciaphila nana* BL. there are here found,

¹⁾ C. L. BLUME. Museum Botanicum Lugduno Batavum I. p. 322. 1849—1851.

²⁾ O. BECCARI. Malesia III. p. 336. Tav. XXXIX. Fig. 5—13. 1886—1890.

³⁾ O. BECCARI. l. c. p. 338.