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

(Communicated in the meeting of January 25, 1913).

§ 1. *Introduction.*

The law of equipartition of energy must hold for the kinetic energy of all systems whose equations of motion <sup>1)</sup> can be represented in the form of the equations of HAMILTON. This is shown in statistical mechanics.

Experiment shows that this law is not fulfilled. This has first clearly appeared from the fact, that the kinetic energy of monatomic and diatomic gases, as it may be derived from the value of  $c_v$ , accounts for only 3 and 5 degrees of freedom respectively, whereas the molecules of these gases have undoubtedly more degrees of freedom, which appears i.a. from the light which they can emit.

Later the observations of NERNST and his disciples have shown, that the  $c_v$  of solids decreases indefinitely when we approach to the temperature  $T = 0$  (absolute) which is also in contradiction with the equipartition law.

Finally we usually deduce from the equipartition law that the partition of the energy over the different wavelengths in the normal spectrum must be as it is indicated by the spectral formula of RAYLEIGH. In this case also experiment shows that the consequences of the equipartition law are not fulfilled in nature.

It appears from the above considerations that we are obliged to assume, that the equations of motion of the real systems cannot have the form of the equations of HAMILTON. The following considerations are to be considered as an attempt to find a way, which may lead to the deduction of the form of the equations of motion of the real systems occurring in nature. In this attempt I will assume that the partition of energy in the normal spectrum is accurately represented by the spectral equation of PLANCK; so I will try to indicate a way which may lead to the drawing up of equations of motion from which the equation of PLANCK can be derived. In consequence of the mathematical difficulties, however, I have not succeeded in finding those equations of motion themselves.

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<sup>1)</sup> With “equations of motion” I mean the equations which are required to reduce the time derivatives of the independent variables by which the condition of a system is determined from the values which these variables have at a given time, independent whether or no these changes refer to motions in the strict sense.

It seems natural to assume, that these equations when they shall have been found, will be able to account for the different above-mentioned deviations from the law of equipartition of energy. In fact these deviations are closely connected with one another. If e.g. the energy of visible light vibrations at  $100^\circ$  is imperceptibly small compared with that of infra-red rays, we cannot wonder that the vibrations of electrons which are in equilibrium with those light vibrations have an energy very small compared with that of vibrations of greater period. The thermal motion of the molecules may here probably be considered as a vibration of rather large period, although it is not a simple harmonic vibration. At a higher temperature the small wavelengths become more predominant in the spectrum. It is therefore to be expected that also the vibrations of the electrons of short period, which at a low temperature are devoid of energy, at a higher temperature will obtain a measurable amount of energy, so that the specific heat with constant volume will increase with the temperature.

The physicists occupied with these problems have noticed this connection between the normal spectrum and the specific heats from the beginning. JEANS<sup>1)</sup> e.g. has applied his theory, which originally was meant to be an explanation of the  $c_v$  of gases, to explain the properties of the normal spectrum; and it is not astonishing that vice versa the theory of PLANCK for the normal spectrum was soon used for the explanation of the specific heats.

The method in which we start from a theory for the normal spectrum and deduce from it the value of  $c_v$  seems to have advantages over the opposite way. For we have in the spectral formula of PLANCK a relation which agrees well with the observations and which moreover is independent of the special nature of the walls. I will therefore follow this method.

## § 2. *The centra of radiation.*

We may make the following two assumptions concerning the way in which the partition of energy of the normal spectrum is brought about.

1st. We may assume that every vibrator considered separately has the property to transform radiation of an arbitrary partition of energy into the partition of energy of the normal spectrum.

2nd. We may assume that this property only belongs to groups

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<sup>1)</sup> J. H. JEANS, Proc. Royal. Soc. of London **67**, p. 236, anno 1900.  
 Phil. Mag. (6) **2**, p. 421 and 638, anno 1901.  
 Proc. Phys. Soc. of London **17**, p. 754, anno 1901, etc.

of vibrators, when their vibration is influenced by their interaction (collisions).

I shall start from the first supposition. In the first place because it is simpler. But it seems to me also to be more plausible. For we cannot doubt that the equations of motion are not linear. A vibrator therefore, when set into vibration by a perfectly homogeneous ray of light, will not execute perfectly harmonic vibrations. The radiation, emitted by it will therefore contain vibrations of other period than the incident ray. If therefore it is inclosed in a space with perfectly reflecting walls it will change the partition of energy of radiation which is also inclosed in that space. If now the spectrum which originates in this manner was not the normal spectrum (because this latter was only brought about by a great many interacting vibrators) it would be astonishing, that even the most rarified gases, in which relatively only a few collisions occur, always give rise to the normal spectrum, and not to a spectrum whose partition of energy lies between the normal spectrum and that of one vibrator.

I will therefore imagine one single vibrator. If its motion was determined by the equation:

$$m \frac{d^2 x}{dt^2} + f x - g \frac{d^3 x}{dt^3} = e \mathcal{E} . . . . . (1)$$

in which the coefficients  $m, f, g, e$  were constants, then it would necessarily give rise to a partition of energy agreeing with the spectral formula of RAYLEIGH<sup>1)</sup>.

Therefore we shall assume from the outset that the equation (1) is not satisfied. The vibrator will then not be able to execute perfectly harmonic vibrations, but its vibrations, when analysed in a series of FOURIER, will consist of several, in general of an infinite number of harmonic vibrations. This seems not to agree with the fact, that undisturbed vibrating vibrators as they occur in gases, emit very sharp spectral lines. We must, however, bear in mind, apart from the fact that no element exists whose spectrum consists in *one* single line, — that according to the electron-theory the mass is not *perfectly* constant and the light of a vibrator therefore not *perfectly monochromatic*. It is true that light of a period  $T$ , differing from the fundamental period  $T_0$  of a vibrator, often occurs only to an imperceptibly small amount in its radiation. But it cannot be totally wanting. Now it is well known that the intensity of radiation of a certain period in the normal spectrum does not depend upon the emission alone, but upon the ratio between emis-

<sup>1)</sup> Comp. H. A. LORENTZ, Nuovo Cimento V, 16. Anno 1908.

sion and absorption, so that a certain wavelength may be represented in the spectrum to its normal amount, even if the emissive power of the walls be imperceptibly small for that wavelength, provided the absorption have a corresponding, small value. The small value of the emissive power has no influence on the final partition. It only occasions that radiation of other energy-partition will only very slowly be transformed into the normal partition.

So we shall assume that the centra of radiation are vibrators whose equations of motion are for the present unknown. These equations cannot have rigorously the form (1), but they need differ only very little from it.

§ 3. *The independent variables. The ensemble.*

We will imagine an ensemble each system of which consists of a parallelepipedic space inclosed in perfectly reflecting walls and containing one vibrator, whose centre has a fixed position in that space. We will assume that the motion of that vibrator is determined by *one* coordinate.

The choice of the independent variables requires a certain circumspection. The aether namely represents an infinite number of degrees of freedom, each of which can therefore possess an infinitely small amount of energy. The vibrator on the other hand possesses a finite amount of energy. It seems, however, difficult to deal with an ensemble in which one variable possesses on an average infinite times as much energy as the other variables. Therefore I will choose the variables as follows: If a monochromatic ray of light passes a vibrator the latter will be set into vibration. After a certain time this vibration will have become stationary. Now I will determine by *one* coordinate the amplitude of the ray and the stationary vibration of the vibrator caused by it.

Besides this I will assume that the vibrator has a "proper" coordinate. Now if this proper coordinate, and also its time derivative are zero, this does not mean that the vibrator stands still in its position of equilibrium. It does mean that the motion of the vibrator consists exclusively of the stationary vibration, which it assumes through the influence of the radiation to which it is subjected. If the proper coordinate is not zero, then the vibrator has a motion which does not agree with the absorbed vibration. So it is possible to assume, that in a radiation field which is in equilibrium (i. e. in which the energy partition is that of the normal spectrum) the proper coordinate of the vibrator has always an infinitely small amount of energy (in the same way as the separate coordinates which determine

the condition of the aether), and that yet the vibrator vibrates with a finite energy the amount of which agrees with that calculated for it by PLANCK<sup>1)</sup>.

We can divide the electromagnetic field into two parts: 1<sup>st</sup> The electrostatic field which agrees with the momentary position of the electron, 2<sup>nd</sup> A field consisting of the really existing electric and magnetic forces diminished by those static forces. In agreement with the above we assume, that the position of the electron and therefore also the 2<sup>nd</sup> field is determined by the first. As for this latter field we have:

$$\text{Div } \mathcal{E} = 0 \quad \text{and} \quad \text{Div } \mathcal{H} = 0,$$

we can represent it as follows, if for simplicity's sake we assume, that the space in which it is inclosed is a cube with a side equal to unity:

$$\left. \begin{aligned} \mathcal{E}_x &= \sum (qa + q'a') \cos 2\pi ux \sin 2\pi vy \sin 2\pi wz \\ \mathcal{E}_y &= \sum (q\beta + q'\beta') \sin 2\pi ux \cos 2\pi vy \sin 2\pi wz \\ \mathcal{E}_z &= \sum (q\gamma + q'\gamma') \sin 2\pi ux \sin 2\pi vy \cos 2\pi wz \\ \mathcal{H}_x &= \sum (p'a + p'a') \sin 2\pi ux \cos 2\pi vy \cos 2\pi wz \\ \mathcal{H}_y &= \sum (p'\beta + p'\beta') \cos 2\pi ux \sin 2\pi vy \cos 2\pi wz \\ \mathcal{H}_z &= \sum (p'\gamma + p'\gamma') \cos 2\pi ux \cos 2\pi vy \sin 2\pi wz \end{aligned} \right\} \dots (2)$$

In the summation we must take for  $2u$ ,  $2v$ , and  $2w$  all positive integers;  $\sqrt{u^2 + v^2 + w^2}$  represents the number of waves in 1 cm. and  $2\pi c\sqrt{u^2 + v^2 + w^2} = \nu$  the number of vibrations in  $2\pi$  seconds. The quantities  $\alpha, \beta, \gamma$  and  $\alpha', \beta', \gamma'$  are the direction coefficients of two directions which are mutually perpendicular, and also perpendicular to the direction determined by  $\frac{u}{\sqrt{u^2 + v^2 + w^2}}, \frac{v}{\sqrt{u^2 + v^2 + w^2}}, \frac{w}{\sqrt{u^2 + v^2 + w^2}}$ .

The quantities  $q, q'$  and  $p, p'$  are the independent variables. One of these variables corresponding to a certain set of values  $u, v, w$  will be represented by  $q_{uvw}$  or  $p_{u,v,w}$ . It can be proved that the variables

<sup>1)</sup> Comp. i. a. MAX PLANCK. Acht Vorlesungen über theoretische Physik. p. 84. In fact our suppositions quite agree with what PLANCK does, when he treats his vibrators as resonators and assumes that their energy is perfectly determined by the radiation field, to which they are subjected. In that case it is however not allowed to equate the entropy of the system to the sum of the amount of entropy of the radiating energy, and that of the vibrator. For the motion of the vibration is perfectly determined by the radiation; the vibrations of the vibrator and of the radiation are therefore coherent and their united entropy is no more equal to the sum of their separate amounts of entropy as this is the case with the entropy of two coherent rays of radiation. (Comp. M. LAUE, Ann. d. Phys. 20 p. 305. 1906; 23 p. 1 and p. 795. 1907 etc.).

$p$  may be considered to be the momenta corresponding to the coordinates  $q$ . As however we must assume that the equations of HAMILTON do not apply, this observation is of no consequence for the equations of motion of the system.

Now if no vibrator occurred in the space, every partition of energy would remain unchanged, and there would be no occasion to speak of an equilibrium partition. If a vibrator occurred which had the property to be able to transform radiation of every wavelength into every other wavelength and whose motion was determined by the equations of HAMILTON, then the energy partition would approach to that indicated by the formula of RAYLEIGH. In this case we might represent the condition of the system by means of an ensemble for which the probability of phase would be represented by <sup>1)</sup>:

$$P = e^{-\frac{\psi - \frac{1}{16} \sum q^2 - \frac{1}{16} \sum p^2}{\theta}} \dots \dots \dots (3)$$

where  $\psi$  and  $\theta$  are constants and  $\frac{1}{16} \sum q^2 + \frac{1}{16} \sum p^2$  is the energy of the system, the summation being extended over all quantities  $q$  and  $p$ , also over those provided with accents.

Properly speaking this expression for the energy is incomplete. In the first place the energy of the proper coordinate of the vibrator has been neglected, but moreover we have neglected the energy of the vibrator, which it has in consequence of its forced vibrations. If we imagine the volume sufficiently large these approximations will meet with no serious objections. More risky is another simplification which I will introduce; I will namely represent an element of extension-in-phase<sup>2)</sup> by  $\Pi dpdq$  and here also I will neglect the proper coordinate (or coordinates if the electron has more degrees of freedom). I think I may suppose that this simplification also will not affect our conclusions greatly. Perhaps it is even perfectly justified. It is namely possible that we must assume, that the motion of the vibrator is entirely determined by the electromagnetic field, and that therefore there is no reason to introduce a "proper" coordinate.

As the spectral formula of RAYLEIGH is not satisfied by the experiments, the formula (3) cannot give the right expression for the probability of phase. I shall therefore put:

<sup>1)</sup> Comp. GIBBS. Elementary principles in statistical mechanics p. 16.

<sup>2)</sup> Comp. GIBBS, l.c. p. 6.

$$P = e^{-\frac{\psi - \frac{1}{16} \sum q^2 - \frac{1}{16} \sum p^2}{\theta}} \varphi(q \dots p). \dots (4)$$

If it is possible to find such a form for the function  $\varphi$  (which represents a function of all variables  $q$  and  $p$ ) that the following formula is satisfied

$$\frac{\int \frac{1}{16} q^2 e^{-\frac{\psi - \frac{1}{16} \sum q^2 - \frac{1}{16} \sum p^2}{\theta}} \varphi(q \dots p) \Pi dq dp}{\int e^{-\frac{\psi - \frac{1}{16} \sum q^2 - \frac{1}{16} \sum p^2}{\theta}} \varphi(q \dots p) \Pi dq dp} = \frac{\theta}{2} \frac{\frac{h\nu}{\theta}}{e^{\frac{h\nu}{\theta}} - 1} \quad (5)$$

then the average energy in the ensemble for every degree of freedom has the value which is indicated for it by the spectral formula of PLANCK. The function of  $\varphi$  must of course have such a form that an equation of the form (5) is satisfied for every variable, not only for the  $q$ 's, but also for the  $p$ 's. The function  $\varphi$  may moreover contain the frequencies  $\nu$ , but it must be independent of  $\theta$ , for else the equations of motion of the system would depend on  $\theta$ , whereas the conception "equation of motion" involves, that they are perfectly determined by the condition of the system at a given instant (the  $q$ 's and  $p$ 's and constants), and that they do not contain a quantity as  $\theta$ , which is not characteristic of the individual system, but of the ensemble. If the condition that  $\varphi$  must be independent of  $\theta$  did not exist, then it would be easy to find several solutions for the integral equations (5). *With* this condition it seems to offer rather great difficulties<sup>1)</sup>.

<sup>1)</sup> The integral equation can in general be brought into the following form:

$$\int e^{-\frac{\frac{1}{16} \sum q^2 - \frac{1}{16} \sum p^2}{\theta}} \varphi(q \dots p) \left\{ \frac{q^2}{8} - \frac{\nu h}{\frac{e^{\frac{\nu h}{\theta}} - 1}{\theta}} \right\} \Pi dq dp = 0.$$

It is possible that  $\varphi$  may be split up into a product of functions  $f(q, \nu)$  each of which contains only one variable and the number of vibrations belonging to it. In this case the equation for the determination of  $f(q, \nu)$  may be written:



Yet I have thought it useful to draw attention to this equation as its solution would be an important step on the way which leads to the drawing up of a system of dynamics from which not the spectral formula of RAYLEIGH, but that of PLANCK would follow.

In this system of dynamics the equations of motion can of course not be brought into the form of HAMILTON. Instead of the law of conservation of density in phase, which follows from this form of the equations of motion, another relation can be derived, which is found as follows. In order that the state is stationary, it is of course required that the probability of phase for a point with constant coordinates is constant. If we indicate the time derivative for such a point with  $\frac{\partial}{\partial t}$ , then we have in the case of equilibrium:

$$0 = \frac{\partial P}{\partial t} = - \sum \left( \frac{\partial P \dot{q}}{\partial q} + \frac{\partial P \dot{p}}{\partial p} \right)$$

or

$$P \sum \left( \frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} \right) = - \sum \left( \frac{\partial P}{\partial q} \dot{q} + \frac{\partial P}{\partial p} \dot{p} \right).$$

It follows from the form of  $P$  that we may also write:

$$\frac{1}{\varphi} \sum \left( \frac{\partial \varphi}{\partial q} \dot{q} + \frac{\partial \varphi}{\partial p} \dot{p} \right) = - \sum \left( \frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} \right) \dots \dots (6)$$

When the function  $\varphi$  is found by solution of the equation (5), then (6) is a relation which the equations of motion must satisfy. It has for the modified mechanics the same significance as the thesis of LIOUVILLE has for classical mechanics.

#### § 4. *The equations of motion of the electrons.*

Though the vibrator does not figure explicitly in equation (6), the values of  $\dot{q}$  and  $\dot{p}$  occurring in it are determined by the properties of the vibrator. For the motion of the electron we can deduce the following equations. We start from the expression for the electrical force of which the  $X$ -component can be represented by:

$$\int_{-\infty}^{\infty} e^{-\frac{1}{16}q^2} f(qv) dq = \frac{4 \sqrt{\pi h v}}{\sqrt{1 - e^{-\frac{v h}{\theta}}}}$$

In the original Dutch paper there is an error in these two formulae and in equation (5), which I have corrected in the English translation.

$$\mathfrak{E}_x = \Sigma (q\alpha + q'\alpha') \cos 2\pi ux \sin 2\pi vy \sin 2\pi wz + m \frac{x}{4\pi r^3}$$

$m$  denoting the electrical moment of the vibrator.

From this expression follows:

$$\frac{d\mathfrak{E}_x}{dt} = c \left( \frac{\partial \mathfrak{H}_z}{\partial y} - \frac{\partial \mathfrak{H}_y}{\partial z} \right) - \rho v_x = \Sigma (q\alpha + q'\alpha') \cos 2\pi ux \sin 2\pi vy \sin 2\pi wz + \frac{x}{4\pi r^3} \frac{dm}{dt}$$

and in connection with (2) and with equations of the form  $v\alpha' = c(v\gamma - w\beta)$ :

$$\Sigma \{ (\dot{q} + vp)\alpha + (\dot{q}' + vp')\alpha' \} \cos 2\pi ux \sin 2\pi vy \sin 2\pi wz = -\rho v_x - \frac{x}{4\pi r^3} \frac{dm}{dt} \dots (7)$$

The divergence of the vector in the lefthand member of this equation is zero, and so also that of the vector in the righthand member. We can therefore represent it by:

$$\Sigma (\sigma\alpha + \sigma'\alpha') \cos 2\pi ux \sin 2\pi vy \sin 2\pi wz.$$

Equation (7) being satisfied identically in  $x, y$  and  $z$ , we have

$$\dot{q} + vp = \sigma \quad \dot{q}' + vp' = \sigma' \dots (8)$$

Differentiating these equations respectively with regard to  $q$  and  $q'$  we get:

$$\frac{\partial \dot{q}}{\partial q} = \frac{\partial \sigma}{\partial q} \quad \frac{\partial \dot{q}'}{\partial q'} = \frac{\partial \sigma'}{\partial q'} \dots (9)$$

If we treat the expressions for the components of  $\mathfrak{H}$  in the equations (2) in the same way, we find:

$$\dot{p} - vq = 0 \quad \dot{p}' - vq' = 0 \dots (8a)$$

and

$$\frac{\partial \dot{p}}{\partial p} = 0 \quad \frac{\partial \dot{p}'}{\partial p'} = 0 \dots (9a)$$

and therefore:

$$-\Sigma \left( \frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} \right) = \frac{1}{\varphi} \Sigma \left( \frac{\partial \varphi}{\partial q} q + \frac{\partial \varphi}{\partial p} p \right) = -\Sigma \frac{\partial \sigma}{\partial q}$$

When  $\varphi$  is known, we can substitute in (10) the values for  $\dot{q}$  and  $\dot{p}$  from (8) and (8a) and so we get a relation which the coefficients  $\sigma$  as functions of  $q$  and  $p$  must satisfy. The value of the  $\sigma$ 's on the other hand depends upon the value of  $q$  as a function of  $x, y$ , and  $z$  and upon the velocities  $\left( v_x \frac{dm}{dt} \text{ in equation (7)} \right)$  which

the electron assumes under influence of the field determined by  $\bar{q}$  and  $\bar{p}$ .

§ 5. *Conclusions.* In the above considerations I have tried to show that it is possible to account for the partition of energy in the normal spectrum with the aid of differential equations, which admit of a continuous emission and absorption of energy, and that it is therefore not necessary for the explanation of the normal spectrum to have recourse to the supposition of quanta, either of energy or of "action". For this explanation it is necessary to draw up a system of mechanics, in which a relation of the form (6) takes the place of the equation of LIOUVILLE in "classical" mechanics. In order to determine this equation further knowledge of the function  $\varphi$  would be required, which function can be found by solution of the integral equation (5). I have however not succeeded in this solution.

If such an explanation with the aid of continuous equations is possible for the partition of energy in the spectrum, then this will also be the case for the variation of the specific heat with the temperature, which follows from this energy partition.

**Chemistry.** — "*Hexatriene 1, 3, 5.*" By Prof. P. VAN ROMBURGH.

(Communicated in the Meeting of February 22, 1913)

In previous communications, published in this Proceedings<sup>1)</sup>, an account was given of the results of an investigation carried out jointly with Mr. VAN DORSSSEN and which had led to the preparation of the above hydrocarbon. Owing to the departure of Mr. VAN DORSSSEN the continuation of the study of hexatriene has experienced considerable delay. Since then, however, a fairly considerable quantity of this substance has been prepared and kept in sealed bottles. As hexatriene — as might be expected from its analogy with other unsaturated compounds (and what also proved to be the case) — exhibited a tendency towards polymerisation particularly on warming, I have submitted the contents of the bottles which had been kept for five years, to investigation.

On distillation fully 50% passed over below 80°: the residue in the flask was then distilled in vacuo. At  $\pm 100^\circ$  about 30% passed over whilst in the flask was left behind a colourless, very viscous mass which dissolves in benzene. From this solution it is again precipitated by acetone or alcohol. If the residue is heated more strongly,

<sup>1)</sup> Nov. and Dec. 1905; June 1906.