

SELECTED PAPERS
ON
WAVE MECHANICS

BY
LOUIS DE BROGLIE

Académie des Sciences, Paris

AND
LÉON BRILLOUIN

Docteur ès Sciences

Authorized Translation by
WINIFRED M. DEANS, B.Sc., B.A.
Late of Newnham College

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PUBLISHERS' NOTE

This translation has been revised by the authors, who have added a few notes. Editorial references to well-known textbooks are enclosed in square brackets.

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Black Radiation and Light Quanta*

BY

LOUIS DE BROGLIE

(*Le Journal de Physique et le Radium*, Vol. 3 (1922), p. 422)

The object of this paper is to establish a number of known results of the theory of radiation by reasoning dependent on thermodynamics, the kinetic theory, and the theory of quanta alone, without the intervention of electromagnetism.

The hypothesis we adopt is that of light quanta. Black radiation in equilibrium at temperature T is considered as a gas formed of atoms of light of energy $W = h\nu$. In this essay we shall neglect molecules of light with 2, 3, . . . , n atoms $h\nu$; that is to say, we ought to arrive at Wien's law of radiation, for, from the point of view of light quanta, Wien's formula is obtained from Planck's general equation † by neglecting associations of the atoms.

In accordance with the formulæ of relativity mechanics, the mass of the atoms of light is taken as equal to $\frac{h\nu}{c^2}$, the quotient of the energy by the square of the velocity of light. Their momentum is $\frac{h\nu}{c} = \frac{W}{c}$. ‡

* This paper was written at the beginning of 1922, two years before the well-known one of S. N. Bose on the light-quanta statistics [*Zeitsch. für Physik*, Vol. 27 (1924), p. 384]; it was the origin of the ideas of the author on wave mechanics.

† [O. W. Richardson, *Electron Theory of Matter*, p. 243; J. H. Jeans, *Report on Radiation and the Quantum Theory*, and *Dynamical Theory of Gases*.]

‡ Relativity dynamics gives $W = m_0 c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right)$ for the kinetic energy of a body of proper mass m_0 moving with velocity $v = \beta c$, and $G = \frac{m_0 v}{\sqrt{1 - \beta^2}}$ for its momentum. If the ratio β is small, we get back to the results of ordinary mechanics, $W = \frac{m_0 v^2}{2}$; $G = m_0 v = \frac{2W}{v}$. For the atom of light, however, m_0 must become infinitely small and β infinitely close to unity in such a way that $\frac{m_0}{\sqrt{1 - \beta^2}}$ has a definite value m . We then have $W = mc^2$ and $G = mc = \frac{W}{c}$: these are the relationships used in the text.

Let n be the number of atoms of light contained in the unit of volume. On unit surface of the boundary, $\frac{1}{6}nc$ atoms of light impinge per second, each of which has momentum equal to $\frac{W}{c}$. The force on unit surface, or the pressure, is therefore $2 \cdot \frac{1}{6}nc \cdot \frac{W}{c} = \frac{1}{3}nW$: it is equal to one-third of the energy contained in unit volume. This result also follows from the electromagnetic theory and has been verified by experiment.

The number of atoms of light of energy W (i.e. of energy between W and $W + dW$) which are situated in the element of volume $dx dy dz$, and the components of whose momentum lie between p and $p + dp$, q and $q + dq$, r and $r + dr$, is given by the following formula of statistical mechanics, which still applies,*

$$dn_W = C e^{-\frac{W}{kT}} dx dy dz dp dq dr,$$

where C is a constant.

To obtain the total number of atoms of energy W we have to integrate throughout the volume, replace $dp dq dr$ by $4\pi G^2 dG$, where G is the length of the vector of momentum, and substitute for G its value $\frac{W}{c}$.

This number of atoms of energy W per unit volume can then be expressed by

$$dn_W = C' e^{-\frac{W}{kT}} W^2 dW,$$

where C' is another constant.

Integration for all values of W from zero to infinity should give the number n of atoms of light per unit volume. This fixes the value of the constant, and we obtain

$$dn_W = \frac{n}{2k^3 T^3} e^{-\frac{W}{kT}} W^2 dW.$$

The total energy du of these atoms of energy W is therefore

$$du_W = \frac{n}{2k^3 T^3} e^{-\frac{W}{kT}} W^3 dW$$

per unit volume.

Let us now attempt to determine n . Let us assume that this number is a function of the temperature only: then this function

* In relativity dynamics the equations of motion are always canonical and Liouville's Theorem is always valid.

can be determined thermodynamically. In fact, the total energy per unit volume is

$$\int_0^\infty du_W, \text{ or } 3nkT,$$

for

$$\int_0^\infty e^{-\frac{W}{kT}} W^3 dW = k^4 T^4 \int_0^\infty e^{-x} x^3 dx = 6k^4 T^4.$$

This result suggests a remark. Each atom of light possesses, on the average, energy $3kT$ and not $\frac{3}{2}kT$ as in the case of the molecules of an ordinary gas, whose velocities are as a rule small compared with the velocity of light. Thus we come back to a fact which the electromagnetic theory explains by the equality of the electric and magnetic energies of a wave of light. This parallelism is reached by using relativity formulæ, which alone allow the exact value of the pressure of radiation, calculated above, to be obtained from the quantum theory of light, whereas the old corpuscular theory of light leads to a value twice the correct one.

The total energy of the gas is therefore $U = 3nkTV$ and the differential of its entropy is

$$\begin{aligned} dS &= \frac{1}{T}(dU + p dV) \\ &= \frac{1}{T}\left(3nkV dT + 3nkT dV + 3kVT \frac{dn}{dT} dT + nkT dV\right), \end{aligned}$$

since the pressure is one-third of the energy per unit volume. Hence

$$dS = \left(\frac{3nkV}{T} + 3kV \frac{dn}{dT}\right) dT + 4nk dV.$$

In order to make dS an exact differential, we must have

$$\frac{3nk}{T} + 3k \frac{dn}{dT} = 4k \frac{dn}{dT}, \text{ or } \frac{dn}{dT} = \frac{3n}{T},$$

the solution of which I write in the form $n = Ak^3 T^3$, A being a constant unknown for the present. This constant is related to Stefan's constant σ , for the energy per unit volume is

$$3nkT = 3Ak^4 T^4,$$

whence, by comparison, $\sigma = 3Ak^4$.

Substituting the value of n in the expression for dS , it becomes

$$dS = 12 Ak^4 T^2 V dT + 4Ak^4 T^3 dV,$$

whence

$$S = 4Ak^4 T^3 V$$

without another constant, since for $T = 0$, $n = 0$, the gas no longer exists.

Since $A = \frac{\sigma}{3k^4}$, we obtain the classical expression $S = \frac{4}{3}\sigma T^3 V$. The free energy $F = U - TS$ can at once be found: it is equal to

$$3nVkT - T \cdot 4nkV = -nVkT = -AVk^4 T^4$$

or to $-NkT$, where N is the total number of atoms in the volume V . There is no constant to be added, since the proper mass of the atoms is nil.*

The quantity of energy which atoms of energy W possess per unit volume is

$$du_W = \frac{A}{2} e^{-\frac{W}{kT}} W^3 dW,$$

and since $W = h\nu$,
$$du_W = \frac{Ah^4}{2} e^{-\frac{h\nu}{kT}} \nu^3 d\nu.$$

Thus we obtain the form of Wien's law. Can we calculate the value of the numerical coefficient in this law (without using the experimental value of σ , of course)?

We can attempt to do so by the method which has enabled Planck, Sackur, Tetrode, and others to calculate the "chemical constant".† We shall follow the argument recently developed by Planck.‡ If a gas consists of N atoms at temperature T , the law of canonical distribution which was proposed by Gibbs and which M. Léon Brillouin has put on a solid basis by utilizing the idea of a thermostat, leads to the formula

$$F = -kT \log \sum_n e^{-\frac{\epsilon_n}{kT}}$$

for the free energy, the sum being taken for all possible states of the gas. This sum can be expressed as an integral taken over the whole phase extension of $6N$ dimensions, an integral which is itself equivalent to the product of N sextuple integrals taken over the phase extension of each molecule, if care be taken, as Planck explains in the article mentioned, to divide the result by $N!$. The theory of quanta introduces the hypothesis of an elementary domain of phase extension of size g ; g has the dimensions of the cube of an action, and the calculation of the chemical constant leads us to set $g = h^3$ (h is Planck's constant).

The expression for F can then be written

$$F = -kT \log \left[\left(\frac{\iiint \iiint e^{-\frac{W}{kT}} dx dy dz dp dq dr}{g} \right)^N \frac{1}{N!} \right]$$

* The thermodynamic potential $U - TS + pV$ is identically zero.

† [H. S. Taylor, *Treatise on Physical Chemistry*, p. 1137.]

‡ *Annalen der Physik*, Vol. 66 (1921), p. 365.

$$\begin{aligned}
 &= -kNT \log \left[\frac{eV}{Ng} \int_0^\infty e^{-\frac{h\nu}{kT}} 4\pi G^2 dG \right] \\
 &= -kNT \log \left[\frac{8\pi eV}{Ng} \times \frac{k^3 T^3}{c^3} \right].
 \end{aligned}$$

We found that $F = -NkT$, no constant being added, since the proper mass of atoms of light is negligible. In order to make the two expressions identical we must have $\log \left[\frac{8\pi eV}{Ng} \frac{k^3 T^3}{c^3} \right] = 1$, whence, since $N = Ak^3 T^3 V$,

$$A = \frac{8\pi}{c^3 g} = \frac{8\pi}{c^3 h^3}.$$

Consequently du_ν becomes

$$du_\nu = \frac{4\pi h}{c^3} e^{-\frac{h\nu}{kT}} \nu^3 d\nu.$$

The expression differs from Wien's law by a factor 2. This difference is not due to a mistake in the calculation, but, as M. Léon Brillouin has pointed out to us, it is probably due to the fact that the idea of the polarization of light was not taken account of in the preceding theory. A more complete theory of light quanta should introduce it in some such form as this: with each atom of light there would be associated an internal state of right-handed or left-handed circular polarization, represented by an axial vector in the direction of the velocity of propagation. Two atoms having the same position and the same velocity, if they were to be regarded as identical in the calculation of F , would further require to be polarized in the same sense (right-handedly or left-handedly); this would introduce a factor 2^N under the logarithm sign in the expression for F , thus restoring the exact value of the numerical coefficient of Wien's law.

By considering a mixture of monatomic, diatomic, triatomic, . . . "gases of light", we should also be able to obtain Planck's law in the form

$$du_\nu = \frac{8\pi h}{c^3} \nu^3 \left[e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + e^{-\frac{3h\nu}{kT}} + \dots \right].$$

This would require some rather arbitrary hypotheses, and we shall not proceed further in this direction.

We can also arrive at the conception of a gas of atoms of light in the following way.

Consider a gas formed of N atoms of "proper mass" m_0 in equilibrium at temperature T . Suppose that relativity dynamics applies to these atoms and neglect all interaction between the atoms:

thus our gas is a perfect gas. The energy and momentum are given by the equations:

$$W = m_0 c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right); \quad \mathbf{G} = \frac{m_0}{\sqrt{1 - \beta^2}} \mathbf{v}; \quad \beta = \frac{v}{c}.$$

Statistical mechanics gives the number dN of atoms whose energy lies between W and $W + dW$ (see above),

$$\begin{aligned} dN_W &= C N e^{-\frac{W}{kT}} G^2 dG \\ &= C N e^{-\frac{W}{kT}} m_0^2 c \sqrt{a(a+2)} (a+1) dW, \end{aligned}$$

putting $\frac{W}{m_0 c^2} = a$ for short. If the mass m_0 is sufficiently large to make

the quotient $\frac{W}{m_0 c^2}$ very small for practically all the atoms (and this is what happens in the case of material gases at ordinary temperatures), we revert to Maxwell's ordinary formula. Suppose, on the contrary, that the mass m_0 is very small; then practically all the atoms will have velocities very close to c : it may indeed happen, if m_0 be small enough, that the number of molecules whose velocity differs from c by more than one-millionth is negligible. In that case a will be much greater than unity, and we can write:

$$dN_W = C' N e^{-\frac{W}{kT}} W^2 dW,$$

a formula from which, as we have seen, the Planck-Wien law is deduced.

The hypothesis of the quantum theory of light should therefore, with the adoption of relativity dynamics, lead us to regard the atoms of light (supposed of the same very small mass) as moving with velocities which vary according to their energy (frequency), but which are all very close to c . We should thus explain why light appears to be propagated (within the limits of experimental precision) with exactly the velocity which in Einstein's formulæ plays the part of infinite velocity.*

Summing up, the essential conclusions of the present paper are as follows:

1. By means of the quantum theory of light, coupled with the rules of statistical mechanics and of thermodynamics, we can re-obtain all the results of the thermodynamics of radiation and even

* The "radiation" of frequency ν would be carried by atoms of mass m_0 , displaced with velocity $c - \frac{c^5 m_0^2}{2\hbar^2 \nu^2}$, the quantity $\frac{c^5 m_0^2}{2\hbar^2 \nu^2}$ escaping experimental detection on account of the smallness of m_0 .

the Planck-Wien law of distribution.* These results, however, expressly assume that the formulæ of relativity dynamics are used for atoms of light.

2. There is no doubt that there is a close connexion between the chemical constant of gases and Stefan's constant for black radiation. This connexion has been set forth already by M. Lindemann in a recent paper on the vapour pressure of solids.† He reveals to us a new aspect of the constant interaction between matter and radiation.

* On the question of light quanta, see Emden, *Phys. Zeitschr.*, **22** (1921), 509; L. de Broglie, *Comptes Rendus*, **175** (1922), 811.

† *Phil. Mag.*, **39**, pp. 21-5.

On the Parallelism between the Dynamics of a Material Particle and Geometrical Optics

BY

LOUIS DE BROGLIE

(*Le Journal de Physique et le Radium*, Vol. 7 (1926), p. 1)

Summary.—By associating the propagation of a wave with the motion of a material particle, the energy and momentum of the particle can be related to the frequency and phase velocity of the wave in such a way that the usual equations of dynamics are derived from a dispersion formula.

The corpuscular theory of light comes up against difficulties when propagation in refracting media is studied; one of these difficulties, which is of great historical importance, relates to a supposed contradiction between the principle of least action and Fermat's law. By deducing the dynamics from the theory of waves, we can consider the question from a new point of view and remove certain objections.

1. Classical Ideas.—The object of this exposition is to show how the ideas about quanta which I have recently developed permit a precise statement to be made as to the parallelism, the existence of which has been indicated for so long, between the dynamics of a particle and geometrical optics.

Let us commence by recalling some outstanding laws of the theory of waves, *without confining ourselves specially to light waves*.

To begin with, I shall give the following general definition: A physical phenomenon is said to be propagated in simple sinusoidal waves, if its mathematical definition involves a sinusoidal function of the co-ordinates of space and time, which is called the phase, and which possesses the two following properties: 1. At a point in space it has period T and frequency $\nu = \frac{1}{T}$. 2. The different values of the phase are displaced in space along certain lines called the "rays of the wave", with a velocity V , which is in general a function of the co-ordinates of space and time as well as of the frequency: this velocity V may also depend on the direction of the ray as looked at from a given point.

In all that follows, I shall for simplicity suppose that the medium is isotropic and in a permanent state. In this case the rays of the wave will have an invariable form and the phase velocity V will be a function of the space co-ordinates and of the frequency alone. We shall express this relationship by the equation

$$n = \frac{c}{V} = \phi(x, y, z, \nu),$$

where c is the classical constant of Maxwell's equations. This equation defines n , the index of refraction.

Besides the velocity V we shall introduce a quantity called "group velocity".* This is defined by supposing that we have not to deal with a simple sinusoidal wave, but with a group of simple sinusoidal waves of nearly equal frequencies comprised within a small interval $\nu - \delta\nu$, $\nu + \delta\nu$. On account of the variation of the refractive index with the frequency, the points where the different simple waves are in the same phase move with a velocity U generally different from V , and a familiar piece of reasoning gives:

$$U = \frac{\partial \nu}{\partial \frac{1}{V}} = c \frac{\partial \nu}{\partial (n\nu)}.$$

The study of electromagnetic waves in accordance with classical ideas shows that the energy carried by one of these waves in general moves with the group velocity, which is always less than, or at most equal to, the constant c .

To calculate the movements of the wave it is sufficient to know the frequency and the function which determines the values of the refractive index. A principle which, in optics, bears the name of Fermat, the great French physicist and mathematician, tells us, in fact, that if a ray passes through two given points A and B, the time taken for the phase to go from A to B is a minimum, or in other words: if the phase followed a path differing slightly from the actual ray, it would take longer to go from A to B. Thus we must write:

$$\delta \int_A^B \frac{dl}{V} = \frac{1}{c} \delta \int_A^B n dl = 0,$$

and, since n is known as a function of x, y, z , the path followed by the ray is determined in this way.

Before we come to my own ideas, let us examine two problems of wave propagation which play a great part in geometrical optics.

* [T. H. Havelock, *Propagation of Disturbances in Dispersive Media* (Cambridge Mathematical Tract).]

(a) *The passage of a wave from a medium of uniform refractive index n_1 to a medium of uniform refractive index n_2 .*

The solution is well known. The ray which goes from the point A of the first medium to the point B of the second is composed of two straight lines which meet at a point M of the surface of separation such that Descartes' law holds:

$$n_1 \sin \alpha_1 = n_2 \sin \alpha_2.$$

(b) *The form of the rays in a refracting sphere, the refractive index of which is a function of the distance from the centre and the frequency alone.*

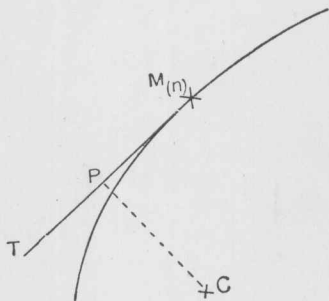
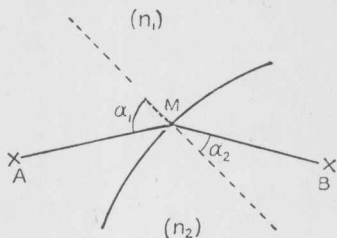
In optics, this problem is called the "problem of astronomical refraction". The form of the rays is given by an equation,* due to Bouguer, which is deduced from the principle of minimum time. If M is any point on the ray to be found, and if MT is the tangent to the ray at that point, the product of the refractive index at the point M and the distance from the centre of the sphere to the tangent MT has a value which is constant all along the ray:

$$np = C.$$

2. **New Hypotheses.**—Up to this point I have confined myself to observations of a classical nature on waves and their rays. I am now going to introduce a hypothesis which is characteristic of my interpretation of quanta. I shall suppose that there is reason to admit the existence, in a wave, of points where energy is concentrated, of very small corpuscles whose motion is so intimately connected with the displacement of the wave that a knowledge of the laws regulating one of these motions is equivalent to a knowledge of the laws regulating the other.

Conversely, I shall suppose that there is reason to associate wave propagation with the motion of all the kinds of corpuscles whose existence has been revealed to us by experiment.

In other respects, I shall in this paper adopt a point of view slightly different from those which I have developed up to now, *for I shall take the laws of wave propagation as fundamental, and seek to deduce from them, as consequences which are*



* [S. Parkinson, *Treatise on Optics*, § 121.]

valid in certain cases only, the laws of the dynamics of a particle.

I therefore take for granted the principle of minimum time, which follows immediately from undulatory conceptions, and I suppose that the relation which gives the value of the refractive index n , at any point and for any frequency, is known. The motion of the wave being thus determined, it is sufficient, in order to deduce from it the motion of an associated corpuscle, to know the expressions which give the energy W and momentum \mathbf{g} of the wave at any point, as functions of n and ν . For reasons explained in my thesis, one hypothesis is absolutely necessary, namely, to set

$$W = h\nu, \quad g = \frac{h\nu}{V} = \frac{h}{c}(n\nu),$$

the vector \mathbf{g} being tangential to the ray along which the phase at the point considered is propagated. Under these conditions, the corpuscle will follow the ray determined by the principle of minimum time $\delta \int n \, dl = 0$, and its trajectory will, in fact, be that found dynamically by applying Maupertuis' principle $\delta \int g \, dl = 0$.

We shall suppose that the velocity of the moving particle is equal to the group velocity of the waves along the ray, and we shall write

$$v = \beta c = U = c \frac{\partial \nu}{\partial (n\nu)} = \frac{\partial W}{\partial g}.$$

Thus our results are still in agreement with mechanics, for, according to Hamilton's equations,* the velocity is the partial differential coefficient of the energy with respect to the momentum. The preceding hypotheses involve the usual form of the fundamental equation of dynamics, for we have:

$$\frac{dg}{dt} = \left(\frac{\partial g}{\partial l} \right)_w \cdot v = \frac{h}{c} \frac{\partial (n\nu)}{\partial l} \cdot c \frac{\partial \nu}{\partial (n\nu)} = h \frac{\frac{\partial (n\nu)}{\partial l}}{\frac{\partial (n\nu)}{\partial \nu}} = -h \frac{\partial \nu}{\partial l} = -\frac{\partial W}{\partial l} = F.$$

3. Dynamics of a Particle.—We have thus established a close connexion between the propagation of the wave and the dynamics of the associated corpuscle. Let us now see if we can deduce from it the particular relations which dynamics postulates between velocity and mass on the one hand, and between energy and momentum on the other hand.

In order to do this we must in each case specify the form taken by the equation of dispersion $n = \phi(x, y, z, \nu)$. Let us first study the

* [E. T. Whittaker, *Analytical Dynamics*, § 109; M. Born, *Mechanics of the Atom*, p. 20; G. Birtwistle, *Quantum Theory of the Atom*, p. 54.]

propagation of a given type of waves in free space at a great distance from any other matter. The following form of the function ϕ is imposed by the principle of relativity:

$$n = \sqrt{1 - \frac{\nu_0^2}{\nu^2}},$$

where ν_0 is an invariant having the same value for all Galilean systems and characteristic of the intrinsic nature of the wave. A corpuscle associated with the wave in the way just specified will have a velocity

$$v = \beta c = c \frac{\partial \nu}{\partial (n\nu)} = nc.$$

Thus, in this case, $n = \beta$, and consequently $V = \frac{c}{n} = \frac{c}{\beta}$, a result which I have proved in many other ways: the energy and the momentum are given by

$$W = h\nu = \frac{h\nu_0}{\sqrt{1 - n^2}} = \frac{h\nu_0}{\sqrt{1 - \beta^2}}; \quad g = \frac{h}{c} (n\nu) = \frac{W}{c^2} v.$$

These forms can be identified with those of Einstein's dynamics by putting

$$h\nu_0 = m_0 c^2,$$

a relation which defines m_0 , the proper mass of the corpuscle, as a function of the invariant ν_0 . If the wave considered is a light wave, the invariant ν_0 and consequently the proper mass m_0 must be taken as extraordinarily small: perhaps, to avoid an objection which M. Langevin has kindly pointed out to me, it would even be better boldly to put $\nu_0 = m_0 = 0$. In any case, the velocity of the corpuscle must be extraordinarily close to the constant c , if not equal to it, and the dynamics of the atom of light appears as a limiting case of the dynamics of a material particle. In particular, it is easy to show that this point of view permits of a complete explanation of the various Doppler effects.

Let us now leave the case of free space and consider a medium with spherical symmetry in which the refractive index varies with the distance r from the centre according to the law

$$n^2 = \left(1 - \frac{F(r)}{\nu}\right)^2 - \frac{\nu_0^2}{\nu^2}.$$

The velocity of an associated corpuscle is here found to be given by

$$v = \frac{nc}{1 - \frac{F(r)}{\nu}} = \beta c.$$