

Below are *very* rough translations of selected sections from the 1906 edition of Max Planck's *Lectures on the Theory of Heat Radiation*. They were prepared in connection with my article on Planck that is to appear in *Physics in Perspective*. In a few places, I have followed translations of Thomas Kuhn, Olivier Darrigol, Allan Needell, and Roger Stuewer, as noted in the article. The translations are frequently very rough indeed, and might aptly be described as being out of the German, but not quite into English; in places, they are all but incomprehensibly literal. I will continue to polish them as time permits. Nevertheless, readers who have any knowledge of German might well want to use these translations together with the German original.

Note that the 1906 edition was never translated into English. It is very different from the second edition of 1913, which is widely available in translation. The 1906 German edition, together with the 1914 translation of the second, appear in Max Planck, *The Theory of Heat Radiation*, with an Introduction by Allan A. Needell (American Institute of Physics, 1988).

Clayton A. Gearhart  
Department of Physics  
St. John's University  
Collegeville, MN 56321  
e-mail: cgearhart@csbsju.edu  
August 2001

#### Fourth Section.

#### Entropy and Probability.

#### **First chapter. Introduction. Fundamental theorems and Definitions.**

**§128.** Since with the introduction of probability considerations into electromagnetic radiation theory an entirely new, for the basis of electrodynamics entirely strange element in the purview of the investigation enters in, then raises itself equally at the beginning of this chapter the principle preliminary questions about the justification and about the necessity of such considerations. One could, that is to say, by superficial considerations easily to the conclusion incline *neigen*, that for probability calculations in a pure electrodynamic theory in general no place would exist. For since the electromagnetic field equations together with the initial and boundary conditions the temporal development of an electrodynamic process unambiguously determines, as is generally known, then would considerations, which stand external to the field equations, in principle unwarranted, but in any case superfluous. Either they lead, that is to say, to the same results as the electrodynamic field equations—then they would be superfluous; or they lead to other results—then they would be incorrect.

In spite of this apparently unavoidable dilemma, there remains *stecken* in these considerations a gap. For the results, to which in the electromagnetic theory of heat the electrodynamic field equations alone lead *genommen fuhren*, are by no means unambiguous, but on the contrary they are ambiguous, and even ambiguous to infinitely

higher order. If we begin to [anknu"pfen], in order to examine/discover [einsehen], to the special in the last chapter considered example, that a resonator of the there considered elementary sort itself in a in after all directions equally radiated vacuum exists. There we drew the conclusion, that in the run of time itself a stationary oscillation state [Schwingungszustand] produces, in which the from a resonator in unit time [Zeiteinheit] absorbed and emitted energy a constant, the intensity  $K_0$  of the it activated monochromatic ray proportional value possessed.[?] But this conclusion we could, as at the beginning of § 122 was explicitly emphasized, only thermodynamically, by no means electro-dynamically established, whereas one from the standpoint of electrodynamic radiation theory must require, that, as all concepts, so also all theorems of heat radiation from purely electrodynamic considerations must be developed. If one only wished to seek, the general connection between the from the resonator absorbed energy and the intensity of the by it [ihn] activated/stimulated ray [Strahlung] entirely without the mixing in [Einmischung] of thermodynamic knowledge from a purely electrodynamic route to derive, then would one soon find, that it does not give such a general connection at all, or in other words, that one over the from a resonator absorbed energy, at given intensity of the [by] it stimulated ray, from the standpoint of pure electro-dynamics in general nothing at all assert, as long as from the values of the amplitudes  $C_n$  and the phase constants  $\theta_n$  of the individual in the stimulated ray containing partial waves nothing further is known. For as well the absorbed energy as also the intensity of the stimulated ray will through certain average values be represented, which from the quantities  $C_n$  and  $\theta_n$  every time in different ways are to be composed, and which therefore not in general from one another can be calculated, no more than, as one could calculate the average value of  $C_n$  from the average value of  $C_n^2$ . Thus if also the intensity of the radiation, which from all sides falls on the resonator, for all spectral regions [Spectralbezirke] as a function of orientation and eventually of time is entirely given, and also the initial state of the resonator is known, so allows itself the oscillations of the resonator from that [daraus] still not unambiguously be calculated, also not approximately, also not for sufficiently long times [Zeitepochen]. On the contrary can the resonator, in the case over the individual values  $C_n$  and  $\theta_n$  are suitably arranged, by the same striking radiation intensity to entirely different kinds of oscillations be caused. [??] Indeed, we will later, in the first chapter of the next section, a special, with all electrodynamic laws entirely compatible process closely discuss, where the resonator, as strange as it sounds, the from all sides on it falling radiation entirely and continually absorbed, without in general ever the smallest amount of energy emitting (§ 172); further thus an other process, where the from a resonator absorbed energy even is negative,<sup>1</sup> where thus the [auffallende] radiation withdraws energy from the resonator, until its energy equals zero! (§ 173).

From a single such example we see, that by the intensity of the stimulated ray the oscillations of a resonator still by no means are determined, and that therefore in a case, where after the laws of thermodynamics and after all experience an unambiguous result is to be expected, the pure electro-dynamics entirely deserted, since for it the presented data not half /not nearly suffices, in order the in the electrodynamic differential equations appearing constants unambiguously to determine.

---

<sup>1</sup> See the note to § 111.

§129. Before we this circumstance and the with it for the electrodynamic theory of heat radiation bound difficulty further pursue, we may draw attention to, that by the mechanical theory of heat, especially the kinetic gas theory, just the same circumstance and the same difficulty exists. For if approximately in a streaming/flowing gas at time  $t = 0$  at each place the velocity, the density, and the temperature is given and in addition the boundary conditions are completely known, then will one after all experience expect, that through it the temporal run of the process is unambiguously determined. But from a purely mechanical standpoint such is by no means the case; for through the visible velocity, the density and the temperature of the gas are still not entirely given the positions and the velocities of all individual molecules, and these one must accurately know, if one from the equations of motion the temporal runoff the process would completely calculate. Thus lets itself here easily be shown, that from the same values of the visible velocity, the density, and the temperature infinitely many well varied [verschiedenartig] processes are mechanically possible, of which a few directly contradict the fundamental laws of thermodynamics, namely the second law.

§130. From these considerations we see, that, if it concerns the calculation of the temporal run of a thermodynamic process, as well the mechanical theory of heat as also the electrodynamic theory of heat radiation with that formulation of the initial- and boundary conditions, which in thermodynamics to an unambiguous determination of the process entirely suffices, by no means comes out [auskommt], but on the contrary that from the standpoint of pure mechanics [bez.] electrodynamics considered still infinitely many solutions of the problem exists.

§131. Now it is very worthy of note that, even if hereafter the definitive proof of different permissible hypotheses first can follow *a posteriori*, one can already through an *a priori* consideration, without supporting itself in any way on thermodynamics, can acquire [gewinnen] a firm basis for the substance [Inhalt] of the asserted [? aufzustellenden] hypothesis. Let us again consider namely the above example (§ 128) that a resonator in a given initial state to a ray of given intensity is exposed [aussetzen]. Then is, as at that time was discussed, the oscillation process in a resonator, so long as one the uncontrollable solitary values [? Einzelwerte] of the  $C_n$  and  $\theta_n$  in the stimulated radiation quite often allows, infinitely many times. But now if one all the infinitely many cases, as they the different by the given radiation intensity possible values of the  $C_n$  and  $\theta_n$  correspond, more closely examined, and the results, to which they individually lead, with one another compared, then one finds, that the enormous majority of these cases in the average values to entirely corresponding results lead, while those cases, in which itself noticeable departures show, only in proportionally vanishing small number occurring, namely then, if certain entirely special exceptional conditions between the individual [einzelnen] quantities  $C_n$  and  $\theta_n$  are satisfied. If one also assumes that such special conditions are not valid [nicht gelten], hence it follows, as different also the constants  $C_n$  and  $\theta_n$  in general may be chosen, for the resonator an oscillation that, if also naturally not in all particulars [Einzelheiten], so still in consideration of all measurable average values—and these are the only ones [einzigen] that can be controlled—a entirely definite can be referred to. [?] And, what now is remarkable is: corresponds in just this way the supported [erhaltene] oscillations to the demands of the second law of

thermodynamics, as in the next chapter [Abschnitt] will be more closely worked out (see § 182).

In mechanics it stands precisely the same. If one, in order to the previous example (§ 129) to return to, all only conceivable positions and velocities of individual gas molecules considers, that with the given values of visible [sichtbaren] velocity [??], the density and the temperature of a gas are compatible, and for each combination of the same the mechanical process exactly after the equations of motion calculated, then one finds likewise, that in the enormous majority of cases processes result, which, if also not in the particulars [Einzelheiten], still in all measurable average values with one another in agreement, and in addition the second law of thermodynamics satisfies.

**§132.** After these considerations it is clear, that the hypotheses, whose introduction above as necessary was demonstrated, their object entirely satisfied, if their contents nothing further signified [besagen], than that such special cases, which special conditions between the individual direct not controllable constants correspond, do not occur in nature. In mechanics this affords [leistet] the hypothesis,<sup>1</sup> that the thermal motions are “molecularly disordered” [“molekular-ungeordnet], in electrodynamics affords the corresponding hypothesis that of “natural radiation,” which means, between the numerous different partial oscillations (179) of a ray no other conditions exist, than those, which through the measurable average values are required (§ 181). If we to the abridgment [? zur Abkürzung] of all states and all processes, for which such an hypothesis is valid, as “elementary disordered” [elementar ungeordnet] designate, then yields the theorem, that *in nature all states and all processes, which contain numerous uncontrollable components, are elementary disordered*, the prerequisite, but also the certain guarantee for the unique/unambiguous determinability [Bestimmbarkeit] of measurable processes, as well in mechanics as in electrodynamics, and at the same time for the validity of the second law of thermodynamics, whereby then self-evidently also for the second law characteristic concept of entropy and the with it immediately connected temperature, its mechanical [or?] respectively [bez.] electrodynamic explanation must find. At the same time it follows, that the concepts of entropy and temperature their essence from the condition of elementary disorder are connected. A purely periodic absolutely plane wave possesses neither entropy nor temperature, because it contains no uncontrollable quantities at all, and thus cannot be elementary disordered, just as the by the motion of an individual motionless [starren] atom is the case. First the irregular interaction of very many partial oscillations of different periods, which themselves independent of one another after the different directions in space propagate, or the unregulated through one another flying about [Durcheinanderschwirren] very many atoms create the preconditions for the applicability of the hypothesis of elementary disorder, and with it for the existence of an entropy and a temperature.

**§133.** But which mechanical or [bez.] electrodynamic quantities describe the entropy of a state? Often these quantities are in some way connected with the “probability” of a state. For since the elementary disorder and the lack of every individual/selective/separate control [Einzelkontrolle] to the essence of entropy belongs,

---

<sup>1</sup> L. Boltzmann, *Lectures on Gas Theory*, 1, p. 21, 1896. Vienna Sitzungsber., 78, June 1878, at the end. See also S. H. Burbury, *Nature*, 51, p. 78, 1894.

then can only combinatoric or probabilistic considerations the necessary starting point for the calculation of these quantities allow. Already the hypothesis of elementary disorder itself is indeed the essence [Wesen] of a probability theorem, since it from an enormous number of equally probable cases a definite number singles out and the same as in nature declares nonexistent.

Since now the concept of entropy, just as the content of the second law of thermodynamics, is a universal, and since on the other hand the theorems of probability possess neither more nor less [nicht minder] universal significance, then is it to be supposed, that the connection between entropy and probability will be very narrow/restricted [enger]. We place therefore our more distant [?? ferneren] remarks to the following theorem to the cusp [?]: *The entropy of a physical system in a definite state depends solely on the probability of this state.* The permissibility and fruitfulness of this theorem will later be shown in different cases. A rigorous general proof of the same will be given but we do not attempt it here. Indeed, such an attempt would obviously in this place not even have a meaning. For as long as the “probability” of a state is not defined numerically, one cannot give a numerical proof of above theorem. One could even perhaps at first glance conjecture, that it on this ground in general has no definite physical content. Nevertheless lets itself be shown through a simple deduction, that one, without on the concept of the probability of a state more closely going into, on the basis of the above theorem, [one] is in the position, the kind of dependence of entropy on probability entirely generally to establish.

**§134.** If we call  $S$  the entropy,  $W$  the probability of a physical system in a definite state, then the above theorem says, that

$$S = f(W), \quad (201)$$

where  $f(W)$  signifies a universal function of the argument  $W$ . If one now may also define  $W$  more closely, as far as lets itself at all events to the mathematical probability concept as established take from [be taken from?], that the probability of a system, which from two from one another entirely independent systems is composed, is equal to the product of the probabilities of both individual systems. If we consider for example as the first system any body on the earth, as the second system a [durchstrahlten] cavity from Sirius, then is the probability for it, that the earthly body in a definite state 1, and at the same time the cavity radiation ?[Hohlraumstrahlung] in a definite state 2 finds itself:

$$W = W_1 \cdot W_2 \quad (202)$$

if  $W_1$  and  $W_2$  are the probabilities for it, that the respective/concerned ?[betreffende] system in the respective state finds itself. If now  $S_1$  and  $S_2$  are the entropies of the individual systems in both states

$$S_1 = f(W_1), \quad S_2 = f(W_2).$$

But from the second law of thermodynamics is the total entropy of the two from one another independent systems:  $S = S_1 + S_2$ , consequently from (201) and (202):

$$f(W_1 W_2) = f(W_1) + f(W_2).$$

From this functional equation lets itself  $f$  be calculated. If one differentiates namely on both sides with respect to  $W_1$ , at constant  $W_2$ , then comes:

$$W_2 \dot{f}(W_1 W_2) = \dot{f}(W_1).$$

If one next differentiates with respect to  $W_2$  at constant  $W_1$ , then comes:

$$f(W_1 W_2) + W_1 W_2 \ddot{f}(W_1 W) = 0$$

or

$$\dot{f}(W) + W \ddot{f}(W) = 0.$$

The most general integral of this differential equation of second order is:

$$f(W) = k \log W + \text{const.} \quad \text{Thus from (201):}$$

$$S = k \log W + \text{const.} \quad (203)$$

by which the dependence of the entropy of the probability is in general determined. The universal constant of integration  $k$  is for an earthly system the same as for a cosmic [one], and if its numerical value is determined, it is valid for both. The second, additive constant of integration has, because the entropy  $S$  contains an arbitrary additive constant, no physical significance, and can be omitted at will.

**§135.** The relationship (203) contains a general method for calculating the expression for the entropy  $S$  through probability considerations. Still will the same naturally first then from practical uses, if the size  $W$  of the probability of a physical system in a given state can be specified numerically. The search for the most general and precise definition of this quantity belongs to the most important tasks of the mechanical or else ?[bez.] electrodynamic theory of heat. To start with, it requires a closer inspection of the concept of the “state” of a physical system.

By the “state” of a physical system at a fixed time we understand the totality of all these from one another independent quantities, through which the temporal run of the in the system taking place processes, so far they are to measurement accessible, by given boundary conditions are uniquely determined; the knowledge of the state is thus just equivalent to the knowledge of the “initial conditions.” There for is for example for a from unchanging molecules composed gas the state determined through the law of space- and velocity distribution, that is through the specification of the number of molecules, whose coordinates and velocity components always [je] within an individual small “interval” or “domain” lie. The to the different domains corresponding numbers of molecules are in general entirely independent of one another, since the state does not need to be an equilibrium or stationary state; they must thus all be individually known, if the state of the gas can be considered as given. On the other hand, is it for the characterization of the state not necessary, the closer details regarding the within an individual elementary domain contained molecule to specify; for here enters the as a supplement the hypothesis of elementary disorder, which in spite of the mechanical uncertainty the uniqueness of the temporal process vouches for.

For a light or heat ray is the state determined through the orientation, the spectral energy distribution, and the polarization state (§ 17). Details over the amplitude and phase of an individual periodic partial wave of a ray is not necessary to now, since also here the hypothesis of elementary disorder as a supplement intervenes.

One sees, that the so definite state concept, in a statistical sense, is well to be distinguished from the state concept in an absolute mechanical or electrodynamic sense, after which is a state first then may be considered as given, if the coordinates and velocity components of each individual molecule, respectively [bez.] the amplitudes and phases of all individual partial waves are accurately known. In such a state would no uncontrollable elements occur and therefore also no probability considerations at all are in place.

**§136.** If we now of the probability  $W$  of a definite elementary disordered state speak, then is with it expressed, that such a state can be realized in different ways. For each state, which contains many similarly uncontrollable constituents, corresponds to a certain “distribution” [“Verteilung”], namely in the first example the distribution of the coordinates and the velocity components of the gas molecules, in the second example the distribution of amplitudes and phases of the individual partial waves. But a distribution is always an allocation [Zuordnung] of a group of among themselves similar elements (coordinates, velocity components, amplitudes, phases) to an other group of among themselves similar elements (molecules, partial waves). As long as one a definite state in eye grasps [or envisions], it manifestly/obviously [offenbar] only depends on how many elements of both groups each other mutually ordered are, but does not depend, on which individual elements of a group are assigned to definite individual elements of the other group. Then can a definite state through a large number of from one another different individual assignments come about. If we thus name each unique distribution, by which the elements of a group are individually associated with the elements of the other group, a “complexion,” then contains a definite state in general a large number of different complexions. This number, that is *the number of complexions, which a given state encompasses, we define as the probability  $W$  of the state*, and obtain by an average, in order in a given case  $W$  and then from (203) the entropy  $S$  of the state to calculate. Closer explanations over the sort of calculation will in the next two chapters come up in detail.

**§137.** Here is only on a point alluded to, in which itself the used definition of probability differs from the otherwise usual definition of the mathematical probability of an event. The last is defined, as is generally known, as a legitimate [echter] fraction, namely as the quotient of the number favorable to the event [divided] by the number of all equally possible [gleichmöglich] cases. In distinction to it [Im Unterschied davon] will here the probability  $W$  of a physical state by a whole number, and to be sure by a large number be expressed. One could attempt, the distinction of the two definitions thereby to remove, that one divides the number of complexions, which encompasses a state, by the number of “all possible” complexions, and this quotient as the probability of the state denotes. By itself it would here by the question after the number of all possible complexions in certain cases [unter Umständen] give rise to difficulties, which we would gladly avoid, as we those questions do not at all raise, and stop [stehen bleiben] with the above given definition of the probability  $W$  of a state. For the calculation of the entropy

will the discussed difference anyway be unimportant, since it after (203) only the addition of an additive negative constant amounts to.

## Second Chapter. Entropy of an ideal monatomic gas.

**§138.** In the previous chapter was the justification and the necessity of the introduction of probability concepts in the mechanical and in the electrodynamic theory of heat demonstrated, and from the general connection of the entropy  $S$  with the probability  $W$ , which is expressed in Equation (203), a method derived, the entropy of a physical system in a given state to calculate. Before this method to the determination of the entropy of radiant heat is applied, will it in this chapter be used, the entropy of an ideal monatomic gas in an arbitrary given state to calculate. All of the essentials of this calculation are to be sure already found in the in part still further ? ausgreifende investigations of L. Boltzmann<sup>1</sup> on the mechanical theory of heat; however/meanwhile [indessen] will it still be recommended, here on that especially simple case especially to go into, once in order the method of calculation and the physical significance of the mechanical entropy with that of radiation entropy conveniently to be able to compare, but then primarily thus, in order the significance of the universal constant  $k$  of Equation (203) in the kinetic gas theory clearly to be allowed to stand out; and in addition suffices naturally treatment of a unique special case.

**§139.** We consider an ideal, consisting of  $N$  monatomic molecules of the same kind gas in a given state and ask after the entropy of the gas in this state. Since the state as given is presumed, then is the law  $f$  spatial and velocity distribution as known assumed (§ 135). If we thus consider the spatial domain, which through the spatial coordinates  $x, y, z$ , and their differentials  $dx, dy, dz$ , and the velocity domain, which through the velocity components  $\xi, \eta, \zeta$  and their differentials  $d\xi, d\eta, d\zeta$  are characterized, then is the number of molecules, whose coordinates and velocities at the same time in these two domains lie, to be considered as given. The extent of such an “elementary domain”:

$$dx \cdot dy \cdot dz \cdot d\xi \cdot d\eta \cdot d\zeta = d\sigma$$

is small compared to the external limits of the entire domain, but nevertheless to be considered large enough, that many molecules are found in it; for otherwise could the state not be elementary disordered. We set therefore the number of the in the elementary domain  $d\sigma$  molecules equal to:

$$f(x, y, z, \xi, \eta, \zeta) \cdot d\sigma \tag{204}$$

$f$  is here as a finite known function of the coordinates and velocity components to be considered, whose analytical expression clearly describes the total/entire [gesamt] partition law and with it the state of the gas. For on the special ordering of molecules within an individual elementary domain it depends no further. [??] We wish  $f$  as continuous and differentiable to assume; in general must  $f$  only the one condition satisfy,

---

<sup>1</sup> L. Boltzmann, Sitzber. D. Akad. D. Wissensch. zu Wien (II) **76**, p. 373, 1877. See also Gas Theory **1**, p.38, 1896.



that itself by integration over all elementary domains yields the total number of gas molecules:

$$f d\sigma = N. \tag{205}$$

**§140.** It concerns now in essence in order the determination of the probability  $W$  for the given spatial and velocity distribution, which from § 136 is equal to the number of complexions which correspond to this distribution. To this goal we first take, what hitherto was not important, all elementary domains  $d\sigma$  as equally large.

Now one can the given spatial and velocity distribution vividly illustrate through it, that one numbers the different equally sized elementary domains, the numerals [Nummern] written next to one another, and under each numeral, set the number of molecules which lies in the concerned domain. If we had for example only 10 molecules and only 7 elementary domains, then would a definite distribution be represented:

1	2	3	4	5	6	7
1	2	0	0	1	4	2

which means that

1 molecule in the	1. elementary domain,
2 molecules “	2. “
0 molecules “	3. “
0 “	4. “
0 “	5. “
4 molecules “	6. “
2 “	7. “ lie.

This definite distribution can now be realized through many different individual orderings or complexions, each according as a definite in the eye fixed molecule in this or in that elementary domain comes to lie. In order a single such complexion to symbolize, one can provide the molecules with digits [Ziffern], write these next to one another, and under each molecule set digit the numeral of that elementary domain, to which the concerned molecule belongs for this complexion. For the above introduced distribution we obtain so as expression of a single to it belonging arbitrarily chosen complexion the following numerical illustration:

1	2	3	4	5	6	7	8	9	10	
6	1	7	5	6	2	2	6	6	7	(206)

This way is expressed, that

The 2. molecule ...	in the 1. elementary domain,
“ 6. & 7. molecules ...	“ 2. “
“ 4. molecule ...	“ 5. “
“ 1., 5., 8., & 9. molecules	“ 6. “
“ 3. & 10. molecules ...	“ 7. “ lie.

As one through a comparison with the previous table immediately perceives, this complexion in fact corresponds in all parts to the above given distribution law, and

likewise allows easily many other complexions to be given, which belong to the same distribution law. The sought number of all possible complexions results now from the consideration of the under both rows of integers (206). For since the number of molecules is given, then contains the row of numerals a definite number of places ? [Anzahl Stellen]. Since further the distribution law is given, then can each numeral (that is, each elementary domain) always appears just so often in the row, as the number of molecules amounts to, which lie in the considered elementary domain. In general requires each change of numeral position [Ziffernbildes] a new individual ordering of molecules to the domain, thus a new complexion. The number of possible complexions, or the probability  $W$  of the given state, is thus equal to the number of under the named conditions possible "permutations with repetition." In the chosen simple numerical example yields therefore after a known form the expression:

$$\frac{10!}{1!2!0!0!1!4!2!} = 37800.$$

The form of this expression is so chosen, that it easily from the here existing [vorliegenden] case of gas molecules can be generalized. The numerator contain the faculty [Fakultät] or factorial of the total number  $N$  of considered molecules, the denominator the product of the faculties [Facultäten] of molecule numbers, which lie in each individual elementary domain, and which in our case through the expression (204) are given.

Therefore we obtain for the sought probability of the given spatial and velocity distribution, and with it of the given state of the gas:

$$W = \frac{N!}{\prod (f d\sigma)!}$$

The symbol  $\Pi$  signifies the product, extended over all elementary domains  $d\sigma$ .

**§141.** From the forgoing it follows from (203) for the entropy of the gas in the given state:

$$S = k \log N! - k \log (f d\sigma)! + const.$$

the summation extends over all elementary domains  $d\sigma$ .

Since  $f d\sigma$  is a large number, then lets itself for the factorial [Fakultät] of the same the Stirling formula be used, which for a large number  $n$  runs in abbreviated form [abgekürzt]:<sup>1</sup>

$$n! = \left( \frac{n}{e} \right)^n \sqrt{2\pi n} . \quad (207)$$

Thus, with the omission of inessential terms,

$$\log n! = n(\log n - 1).$$

Therefore, using  $f d\sigma$  instead of  $n$ :

---

<sup>1</sup> See for example B. E. Czuber, *Calculus of Probability [Wahrscheinlichkeitsrechnung]* (Leipzig, B. G. Teubner), p. 22, 1903.

$$S = k \log N! - k \int f d\sigma [\log f d\sigma - 1] + \text{const.}$$

The summation sign we replace from now on by an integral sign. Further we will consider all additive constant terms in the const absorbed. To that belongs first the term with  $N!$ , in addition the factor  $d\sigma$  behind the logarithm, because all elementary domains are equally large, and because  $\int f d\sigma = N$  is constant, finally the term with  $-1$ . Then remains for the entropy of the gas the remaining expression:

$$S = \text{const} - k \int f \log f d\sigma, \quad (208)$$

valid for any arbitrarily given space and velocity distribution of the gas molecule, thus for each state of the gas.

**§142.** We will now specifically determine the entropy of the gas in an equilibrium state, and ask therefore first after that form of the distribution law, which corresponds to thermodynamic equilibrium. From the second law of thermodynamics is an equilibrium state distinguished by the condition, that for given values of the total volume  $V$  and the total energy  $U$ , the entropy  $S$  takes on its maximum value. If we thus set the total volume of the gas molecule [to]:

$$V = \int dx dy dz$$

and the total energy of the same [to]:

$$U = \frac{m}{2} \int (\xi^2 + \eta^2 + \zeta^2) f d\sigma \quad (209)$$

as given previously [voraus] ( $m$  the mass of a molecule), then must for the equilibrium state the condition hold:

$$\delta S = 0$$

or from (208):

$$(\log f + 1) \delta f d\sigma = 0, \quad (210)$$

where the variation  $\delta f$  itself to an arbitrary with the given values of  $N$ ,  $V$ , and  $U$  compatible change of the distribution law refers to.

Now is because of the constant number  $N$  of gas molecules from (205):

$$\delta f d\sigma = 0$$

and because of the constant total energy  $U$  from (209):

$$(\xi^2 + \eta^2 + \zeta^2) \delta f d\sigma = 0.$$

Consequently is to the realization [Erfüllung] of the condition (210) for all permitted  $\delta f$  necessary and sufficient, that

$$\log f + \beta(\xi^2 + \eta^2 + \zeta^2) = \text{const}$$

or

$$f = \alpha e^{-\beta(\xi^2 + \eta^2 + \zeta^2)}, \quad (211)$$

with  $\alpha$  and  $\beta$  constant. Thus in the equilibrium state is the spatial distribution of the molecule uniform, that is, independent of  $x$ ,  $y$ ,  $z$ , and the velocity distribution is the known Maxwellian.

**§143.** The values of the constants  $\alpha$  and  $\beta$  follow from those of  $N$ ,  $V$ , and  $U$ . For the substitution of the found expression for  $f$  in (205) results in:

$$N = V \alpha \int_{-\infty}^{+\infty} e^{-\beta(\xi^2 + \eta^2 + \zeta^2)} d\xi d\eta d\zeta = V \alpha \left( \frac{\pi}{\beta} \right)^{3/2}$$

and the substitution of  $f$  in (209) results in:

$$U = V \frac{m}{2} \alpha \int_{-\infty}^{+\infty} (\xi^2 + \eta^2 + \zeta^2) e^{-\beta(\xi^2 + \eta^2 + \zeta^2)} d\xi d\eta d\zeta$$

$$U = \frac{3}{4} V m \alpha \frac{1}{\beta} \left( \frac{m}{\beta} \right)^{3/2}.$$

It follows that:

$$\alpha = \frac{N}{V} \left( \frac{3mN}{4\pi U} \right)^{3/2}, \quad \beta = \frac{3mN}{4U}$$

and finally following from (208) the expression for the entropy  $S$  of a gas in the equilibrium state at given values of  $N$ ,  $V$ , and  $U$ :

$$S = \text{const} + kN \left( \frac{3}{2} \log U + \log V \right). \quad (212)$$

Here the additive constant contains terms with  $N$  and  $m$ , but not with  $U$  or  $V$ .

**§144.** The here led through determination of the entropy of a monatomic gas depends only on the general by Equation (203) expressed connection between entropy and probability; in particular, we have by our consideration in no place made use of any special theorem of the theory [Lehre] of gases. Therefore it is of importance to see, how now from the found expression for entropy the entire thermodynamic behavior of a monatomic gas, namely the general thermodynamic definition equation for entropy:

$$dS = \frac{dU + p dV}{T} \quad (213)$$

results from the partial derivatives of  $S$  with respect to  $U$  and  $V$ :

$$\left( \frac{\partial S}{\partial U} \right)_V = \frac{1}{T}, \quad \left( \frac{\partial S}{\partial V} \right)_U = \frac{p}{T}.$$

It follows for our gas, with the use of (212):

$$\left( \frac{\partial S}{\partial U} \right)_V = \frac{3}{2} \frac{kN}{U} = \frac{1}{T} \quad (214)$$

and

$$\left( \frac{\partial S}{\partial V} \right)_U = \frac{kN}{V} = \frac{p}{T}. \quad (215)$$

The second of these two equations:

$$p = \frac{kNT}{V}$$

embodies the laws of Boyle, Gay Lussac, and Avogadro, and the last therefore, because the pressure depends only on the number  $N$ , not on the character of the molecule. If one writes it in the usual form:

$$p = \frac{RnT}{V},$$

where  $n$  the number of gram molecules or moles of the gas, based on  $O_2 = 32$  g, and  $R$  signifies the absolute gas constant:

$$R = 8.31 \cdot 10^5 \frac{\text{erg}}{\text{degree}}, \quad (216)$$

then it follows by comparison:

$$k = \frac{Rn}{N}. \quad (217)$$

If we call  $\omega$  the ratio of the number of molecules to the number of moles, or, what is the same thing, the ratio of the molecular mass to the molar mass,  $\omega = \frac{n}{N}$ , then it follows:

$$k = \omega R. \quad (218)$$

From this one can, if  $\omega$  is given, calculate the universal constant  $k$ , and invert.

Equation (214) becomes [lautet]:

$$U = \frac{3}{2} kNT. \quad (219)$$

Since now, on the other hand, the energy of an ideal gas:

$$U = Anc_v T,$$

where  $c_v$  signifies the heat capacity in calories of a mole at constant volume, and  $A$  the mechanical equivalent of heat:

$$A = 419 \cdot 10^5 \frac{\text{erg}}{\text{cal}}, \quad (220)$$

then it follows:

$$c_v = \frac{3 kN}{2 An}$$

and by consideration of (217):

$$c_v = \frac{3 R}{2 A} = \frac{3}{2} \cdot \frac{831 \cdot 10^5}{419 \cdot 10^5} = 3.0 \quad (221)$$

as the molar heat [Molwärme] in calories of any monatomic gas at constant volume.<sup>1</sup>

For the molar heat  $c_p$  at constant pressure, it follows from the first law of thermodynamics that:

$$c_p - c_v = \frac{R}{A},$$

thus in consideration of (221):

$$c_p - c_v = \frac{2}{3} c_v, \quad \frac{c_p}{c_v} = \frac{5}{3},$$

which is well known for monatomic gases.

The average energy or the average kinetic energy  $L$  of a molecule from (219) results in:

$$\frac{U}{N} = L = \frac{3}{2} kT. \quad (222)$$

One sees, that all of these relationships follow [sich ergeben] solely from the identification of the mechanical expression (208) with the thermodynamic expression (213) for the entropy.

### Third Chapter Calculation of the radiation energy and consequences from it. Energy partition law. Elementary quanta.

**§145.** After we have seen, how one can calculate for an ideal gas the expression for entropy directly from the probability of the state, and how itself from it all thermodynamic properties of the gas through a direct application of the laws of thermodynamics can be deduced (derived?), we will now carry through (durchführen) the same train of thought for radiant heat. From Wien's displacement law we obtained in

<sup>1</sup> See F. Richarz, *Wied. Ann.* **67**, p., 705, 1899.

Equation (119) an expression for the spatial entropy density  $S$  as a function of the spatial energy density  $u$ , further in Equation (134) an expression for the spatial entropy density  $s$  of an individual ray as a function of its specific intensity  $K$ , finally in Equation (200) an expression for the entropy  $S$  of a resonator exposed to thermal radiation as a function of its energy  $U$ . Each of these three expressions contains an up to now still unknown remaining universal function of a single argument, and the calculation of this function is in the following arrived at. If this problem for one of the three named expressions is solved, are with it also the two other expressions found, by virtue of the known earlier connections between the quantities  $s$ ,  $L$ , and  $S$  among themselves, and the quantities  $u$ ,  $K$ , and  $U$  among themselves. We can therefore from the outset begin with any of these three equations. For the most part recommends itself naturally (or, it is naturally advisable) the simplest of them to choose, and that is, as already earlier emphasized, the resonator equation (200):

$$S = F\left(\frac{U}{v}\right), \quad (223)$$

if we the oscillation frequency of the characteristic period of the resonator from now on denote briefly with  $v$  without an index. The function  $F$  contains except for its argument only universal constants.

**§ 146.** In connection with the closer investigation of the entropy of a resonator of given energy, the first question is after the kind of elementary disorder, on which the entropy depends and without which it possesses no significance (§ 132). A glance at Equations (187) and 195 gives the answer. According to them are the oscillations of an to thermal radiation exposed resonator composed from a large series of partial oscillations, and its energy is an average value from very many in particular/individually ? [im einzelnen] not controllable quantities. These numerous from one another independent partial waves are thus it, which play the same role by the resonator with regard to elementary disorder, which for a gas is due to the numerous molecules moving about pell-mell. Thus one can say little about a gas of a finite entropy, if all molecules have equal and equally directed velocities, or in any other way have ordered velocities, just as little comes to a resonator a finite entropy, if its oscillations are nearly simply periodic or if they in general follow any definite law at all, which governs everything in particular ?? [das alles bis ins einzelne regelt.] For then is the oscillation process no longer elementary disordered. Therefore possesses for example a resonator, which is not in general agitated from outside, no finite entropy and no finite temperature, even if it can have a finite energy.

Whether or not the resonator oscillations are elementary disordered, can one often not at all judge, if one considers the state of a resonator only at a fixed instant. For then remains it still entirely undetermined, whether the state changes regularly or irregularly with time. Thus agrees entirely with it, that we the energy  $U$  of a resonator exposed to stationary thermal radiation can only define as a time average, as in § 123 occurred ? [geschehen ist]. On this basis thus the entropy of a resonator possesses significance not for an instant but only for a time interval, which contains many resonator oscillations, and

we can only speak of a time average of the entropy.<sup>1</sup> Briefly said: by the thermal oscillation of a resonator is the disorder temporal, while it for the molecular motion of a gas is spatial. However falls this distinction for the calculation of the entropy of a resonator not so important, as it perhaps at first glance might appear; for it lets itself through a simple consideration be removed, what in the interest of a uniform treatment of advantage is.

The time average  $U$  of the energy of an individual in a stationary radiated vacuum situated resonator is of course evidently identical with the at a fixed instant taken average value of the energies of a very large number  $N$  of equally constituted resonators, which find themselves in the in the same stationary radiation field, but so far removed from one another, that their oscillations are not perceptibly affected. Naturally must to this goal the field of sufficiently spatial extension be taken. With it is the question after the partition of energy among the individual partial waves of a single resonator reduced to the spatial partition of energy among the  $N$  resonators, as better corresponds to the treated case in connection with gas molecules.

§ 147. In order to calculate now the entropy of this system of  $N$  equally constituted resonators in a given state in a stationary radiation field existing, we must to begin with, following the argument of § 135, ask after that quantity, which determines the physical state of the system. That is here purely and simply [einzig und allein] the average energy  $U$  of a single resonator, or rather the total energy  $U_N$  of the entire system of resonators, which is related to  $U$  by the equation:

$$NU = U_N \quad (224)$$

For since/if [da] the radiation field is stationary, then the physical state of the entire system is determined by the energy. In this point lies the most important distinction between the case considered here, and the earlier case of a gas. For there the state was restricted [bedingt] by the kind of spatial and velocity distribution among the molecules, which could be taken as entirely random. Only if the distribution law were first given, could the state be taken as known. Here by contrast the specification of the total energy  $U_N$  of the  $N$  resonators suffices for the determination of the state; the special kind of distribution of the energy  $U_N$  among the separate Resonators is no longer subject to regulation [Kontrolle], it is left entirely to chance, to elementary disorder. For the condition that the radiation field is stationary does not signify here [? nicht etwa] a special case among many others, but on the contrary, belongs with the necessary assumptions; otherwise one could no longer identify the quotient  $U_N / N$ , as we have done, with the time average of the energy of a single resonator.

§ 148. It is moreover ? [nun weiter] a question of the probability  $W$  of the through the energy  $U_N$  determined state of  $N$  resonators, that is of the number of individual assignments or complexions, which corresponds to the distribution of the energy among the  $N$  resonators (§ 136). We can proceed here in full analogy with gas molecules, if only we bear in mind that the given state of the resonator system does not, as there, admit of a

---

<sup>1</sup> In connection with the application to nonstationary fields must the time interval on which the average is based be taken so small that the field can be considered as stationary.



single distribution law, but on the contrary a large number of different ones, since the number of resonators that possess a definite amount of energy (better: which fall in a definite “energy domain”) is not prescribed, but on the contrary can vary. If we consider all possible kinds of energy distribution laws and calculate for each one the corresponding number of complexions, just as with gas molecules, then we obtain by addition of all of the so-obtained complexions, the sought probability  $W$  of the given physical state.

We come faster and easier than by the indicated path to the same goal as follows. We divide the given total energy  $U_N$  into a large number  $P$  of equal parts of the size  $\epsilon$ , which we call an energy element. Then is

$$P = \frac{U_N}{\epsilon}. \quad (225)$$

These  $P$  energy elements are divided in all possible ways among the  $N$  resonators, but in doing so, it is not of importance, which energy elements, but on the contrary only how many energy elements are allotted to a given resonator. If we thus consider the  $N$  resonators numbered and the numerals written next to one another in a row that corresponds to the respective resonator, and to be sure each numeral as often, as the number of energy elements comes to, then we obtain through such a row of numerals the picture of a definite complexion, in which each individual resonator received a definite energy. The order of numerals in a row is for the complexion indifferent, since a mere transposition of numerals does not alter the energy of a specific resonator. If in the complexion a resonator possesses no energy at all, then its numeral does not appear at all in the row. Accordingly the number of all possible different complexions equals the number of possible “combinations with repetitions of  $N$  elements up to/of the  $P$ th order/rank”: [? zur P. Klasse]

$$W = \frac{(N + P - 1)!}{(N - 1)! P!}$$

and this is at the same time the sought probability of the given state of  $N$  resonators. If for example  $N = 3$ ,  $P = 4$ , than are the pictures of all possible complexions:

1 1 1 1	1 1 3 3	2 2 2 2
1 1 1 2	1 2 2 2	2 2 2 3
1 1 1 3	1 2 2 3	2 2 3 3
1 1 2 2	1 3 3 3	2 3 3 3
1 1 2 3	1 3 3 3	3 3 3 3

The number of all possible complexions is here  $W = 15$ , in conformity with the formula.

For the entropy  $S_N$  of the resonator system we obtain after Equation (203), since  $N$  and  $P$  are large numbers, with the omission of the additive constant:

$$S_N = k \log \frac{(N + P)!}{N! P!}$$

and with the use of the Sterling formula (207):

$$S_N = kN \left\{ \left( 1 + \frac{U}{\varepsilon} \right) \log \left( 1 + \frac{U}{\varepsilon} \right) - \frac{U}{\varepsilon} \log \frac{U}{\varepsilon} \right.$$

and for the entropy of an individual resonator:

$$S = \frac{S_N}{N} = k \left\{ \left( 1 + \frac{U}{\varepsilon} \right) \log \left( 1 + \frac{U}{\varepsilon} \right) - \frac{U}{\varepsilon} \log \frac{U}{\varepsilon} \right. .$$

A comparison of this expression with (223) shows, that the energy element  $\varepsilon$  must be proportional to the oscillation frequency  $\nu$  of the characteristic period of a resonator. We therefore set

$$\varepsilon = h\nu , \tag{226}$$

where  $h$  is constant, and thereby obtain

$$S = k \left\{ \left( 1 + \frac{U}{h\nu} \right) \log \left( 1 + \frac{U}{h\nu} \right) - \frac{U}{h\nu} \log \frac{U}{h\nu} \right. \tag{227}$$

as the solution of the treated problem.

**§ 149.** Conspicuous in this result is first of all the appearance of a new universal constant  $h$  with the dimensions of the product of energy and time. Herein lies an important difference compared to the expression for the entropy of a gas, where the size of an elementary domain, which we called  $d\sigma$ , disappears from the final result, since it affects [geltend macht] only a physically meaningless additive constant. There can be no doubt that the constant  $h$  plays an undoubted [gewisse] role at an emission center of the elementary oscillation process, for the explanation of which from the electrodynamic side our hitherto existing theory affords no closer foothold.<sup>1</sup> And yet the thermodynamics of radiation will have arrived at an entirely satisfactory conclusion, only when the constant  $h$  is understood in its full universal significance. I may call it the “elementary action quantity/quantum” or “action element,” because it is of the same dimensions as that quantity, to which the principle of least action owes its name.

**§ 150.** It is of interest to make especially certain, that one [is led?] to the same expression for entropy as arrived at above, if in connection with [bei] the calculation of the number of complexions that correspond to a given state, one refers not at the outset to the energy, which is after all a compound quantity, but on the contrary goes back directly to the electromagnetic state of individual resonators, for which the calculation is not quite as simple, but more general and therefore more rational. It is essentially a question of the correct measurement of the “elementary domain” of the state area [Zustandbereich], [da?] whose size the calculation of the complexions will certainly be based upon, and

---

<sup>1</sup> See the note in § 109.

consequently in the last analysis the measure furnished for the comparison of the probability of different states. The electromagnetic state of a resonator is after § 104 determined by the value of  $f$  and  $f'$ . Thus if one traces in a coordinate plane  $f$  as abscissa and  $f'$  as ordinate, then each point of the plane corresponds to a specific state of the resonator, and vice-versa. The size of a surface element in this plane is by no means in general a measure of the probability, that the state of a resonator will be described by a point within the surface element. On the contrary, this simple theorem is valid only if instead of  $f'$  as ordinate, one takes the “impulse” coordinate corresponding to  $f$  (or the “momentum” of  $f$ ), namely the quantity

$$\frac{\partial U}{\partial \dot{f}} = g$$

that is, following [Eq.] (142):<sup>1</sup>  $g = L\dot{f}$ . (228)

Let us consider  $f$  and  $g$  as the coordinates of a point of the state plane, and ask first for the magnitude of the probability that the energy of a resonator lies between the values  $U$  and  $U + \Delta U$ . This probability is measured by the size of the elementary area [Flächenstücks] in the plane of the state variables  $f$  and  $g$ , which is bounded by the curves  $U = \text{const}$  and  $U + \Delta U = \text{const}$ .

The energy of a resonator in the state point  $(f, g)$  is from (142) and (228) now given by

$$U = \frac{1}{2} K f^2 + \frac{1}{2} \frac{g^2}{L},$$

consequently the curve  $U = \text{const}$  is an ellipse with the semi-major axes:

$$\sqrt{\frac{2U}{K}} \quad \text{and} \quad \sqrt{2UL}.$$

Hence its surface area comes to:

$$\pi \sqrt{\frac{2U}{K}} \sqrt{2UL} = 2\pi U \sqrt{\frac{L}{K}} = \frac{U}{\nu},$$

if one following Equation (166) introduces the oscillation frequency  $\nu$  of the characteristic period of a resonator. In the same way it follows that the surface area of the ellipse  $U + \Delta U = \text{const}$ . is:

$$\frac{U + \Delta U}{\nu}.$$

The difference between the two areas, the measure of the sought probability, thus amounts to  $\frac{\Delta U}{\nu}$ . If we now consider the entire state plane divided into separate

---

<sup>1</sup> See for example L. Boltzmann, Gastheorie II, p. 62ff., 1898, or J. W. Gibbs, Elementary Principles in Statistical Mechanics, Chapter I, 1902.

segments by a large number of such ellipses, so that the the annular elementary areas [Flächenstücke] bounded by each two successive ellipses are equal, so that

$$\frac{\Delta U}{\nu} = \text{const} ,$$

we then obtain thereby each segment  $\Delta U$  of the energy which corresponds to equal probabilities, and which therefore are to be designated as energy elements. If we set the size of an energy element  $\Delta U = \varepsilon$  and the constant of the last equation to  $h$ , then we return exactly to the earlier Equation (226), without bringing up Wien's Distribution Law. At the same time the elementary quantum of action  $h$  appears in a new significance, namely as the size of an elementary domain in the state-plane of a resonator, valid for resonators of entirely arbitrary oscillation period. The condition that the constant  $h$  is introduced as a specific finite size is characteristic of the entire theory developed here. If one were to take  $h$  as infinitely small, then one would come to a radiation law, which arises as a special case from the more general (the Rayleigh Law, see § 154 and especially § 166).

§ 151. Equation (227) leads first in consideration of (198) and (193) to the expression for the radiation entropy  $L$  of a monochromatic linearly polarized ray of specific radiation intensity  $K$  and frequency  $\nu$ :

$$L = \frac{k\nu^2}{c^2} \left\{ \left( 1 + \frac{c^2 K}{h\nu^3} \right) \log \left( 1 + \frac{c^2 K}{h\nu^3} \right) - \frac{c^2 K}{h\nu^3} \log \frac{c^2 K}{h\nu^3} \right\} \quad (229)$$

as the definite formulation [? bestimmt Fassung] for Equation (134) of Wien's distribution law.

In addition it follows in consideration of (197) and (194) the spatial entropy density  $S$  of a uniform monochromatic unpolarized ray in its dependence on the spatial energy density  $u$ :

$$S_\nu = \frac{8\pi k\nu^2}{c^3} \left\{ \left( 1 + \frac{c^2 u_\nu}{8\pi h\nu^3} \right) \log \left( 1 + \frac{c^2 u_\nu}{8\pi h\nu^3} \right) - \frac{c^2 u_\nu}{8\pi h\nu^3} \log \frac{c^2 u_\nu}{8\pi h\nu^3} \right\} \quad (230)$$

as the definite formulation [?] of Equation (119).

§ 152. We will not in each of the three equations (227), (229), (230) the temperature  $T$  of the resonators respective of [? bez.] the monochromatic radiation introduce and the energy quantities  $U$ ,  $K$  and  $u$  express. We use one of the equations (199), (135), and (117), and obtain:

For the energy of the resonator:

$$U = \frac{h\nu}{e^{kT} - 1} . \quad (231)$$

For the specific intensity of a linear monochromatic polarized ray of frequency  $\nu$ :

$$K = \frac{h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}. \quad (232)$$

For the spatial energy density of a linear monochromatic unpolarized ray of frequency  $\nu$ :

$$u = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}. \quad (233)$$

If one relates the specific intensity of a monochromatic ray not to the frequency  $\nu$  but to the wavelength  $\lambda$ , as usually happens in experimental physics, then one obtains with the use of (15) and (16) the expression:

$$E_\lambda = \frac{c^2 h}{\lambda^5} \frac{1}{e^{\frac{ch}{k\lambda T}} - 1} \quad (234)$$

as the intensity of a monochromatic linearly polarized ray of wavelength  $\lambda$ , which from a of the temperature  $T$  ...

§ 153. For small values of  $\lambda T$  (that is, small compared to the constant  $\frac{ch}{k}$ ), goes (234) over into the equation:

$$E_\lambda = \frac{c^2 h}{\lambda^5} e^{-\frac{ch}{k\lambda T}}, \quad (235)$$

which states the “Wien energy distribution law.”

The specific radiation intensity  $K$  will then after (232):

$$K = \frac{h\nu^3}{c^2} e^{-\frac{h\nu}{kT}} \quad (236)$$

and the spatial energy density  $u$  after (233):

$$u = \frac{8\pi h\nu^3}{c^3} e^{-\frac{h\nu}{kT}}. \quad (237)$$

For the energy of a resonator of frequency  $\nu$  one obtains from (231):

$$U = h\nu e^{-\frac{h\nu}{kT}}. \quad (238)$$

for the entropy  $S$  of a resonator as a function of the energy  $U$  will after (227), since the quotient  $\frac{U}{h\nu}$  assumes small values:

$$S = -\frac{kU}{h\nu} \log \frac{U}{eh\nu}. \quad (239)$$

These conditions thus hold for every wavelength at sufficiently low temperatures, and for every temperature at sufficiently short wavelenth.

§ 154. For large values of  $\lambda T$  on the other hand will from (234):

$$E_\lambda = \frac{ckT}{\lambda^4}, \quad (240)$$

a relation that was first set forth by Lord Rayleigh, and that we therefore can call as the “Rayleigh Radiation Law.”

For the specific intensity  $K$  there results from (232):

$$K = \frac{hv^2T}{c^2} \quad (241)$$

and for the energy density  $u$  of a monochromatic ray from (233):

$$u = \frac{8\pi kv^2T}{c^3}. \quad (242)$$

The energy of a resonator will be after (231):

$$U = kT, \quad (243)$$

thus simply proportional to the absolute temperature and entirely independent of the oscillation frequency  $\nu$  of the characteristic period, as in general from the natural state of a resonator.

For the entropy  $S$  of a resonator as a function of its energy  $U$  we finally obtain under the same assumption, since  $\frac{U}{hv}$  takes on large values :

$$S = k \log U + const. \quad (244)$$

It is of interest, to compare the simple for long wavelengths or high temperatures valid result (243) of oscillation energy of a resonator, with the earlier in (222) calculated average kinetic energy  $L$  of motion of a monatomic molecule at the same temperature. The comparison yields:

$$U = \frac{2}{3}L. \quad (245)$$

This relationship, and with it also the identity of the constant  $k$  for molecular motion and for radiation processes, is confirmed from an entirely different side in very noteworthy ways through a consequence of electron theory. From the views[??] of this theory has one namely the by us considered linear vibrations of an elementary oscillator set forth as rectilinear motion of an electron. Then must after a theorem of statistical mechanics in a by thermal radiation filled gas by thermodynamic state of equilibrium the average kinetic energy of this rectilinear electron motion equal be to the third part of the average kinetic energy of the translational [?] motion of a molecule; for the last motion will through three from each other independent components be determined, possess thus three degrees of freedom, while against it the electron oscillations equal to half of the entire vibrational energy, thus  $\frac{1}{2} U$ , on the other side is the third part of the average kinetic energy of the translational motion of a molecule equal to  $\frac{1}{3} L$ , thus following from the condition

(245). If the different resonators with different natural frequencies in a gas exist, then must they all possess the same average vibrational energy, even so as the average kinetic energy of translational motion of different kinds molecules is the same. In fact  $U$  is after (243) independent of  $v$ .<sup>1</sup>

**§ 165.** An additional interesting confirmation of the radiation law of black bodies for long wavelengths and the connection of the radiation constant  $k$  with the absolute mass of a ponderable molecule has recently been discovered by J. H. Jeans,<sup>2</sup> from a previously explored [?] path by Lord Rayleigh,<sup>3</sup> which differs essentially from that taken [?] here, in that he entirely avoids drawing on special interactions between matter (molecules, oscillators) and aether, and in essence takes up only processes in the irradiated vacuum. The following theorem of statistical mechanics (see above, § 154) affords the starting point of this way of thinking. If irreversible processes take place in a system obeying Hamilton's equations of motion, whose state is determined through the values of a large number of independent variables, and whose total energy is additively composed of quadratically dependent terms of the different individual state variables, then if these take place on average always in the direction, that the corresponding partial energies from the individual independent state variables mutually equalize, so that eventually, by reaching statistical equilibrium, all on average have become equal to each other. Thus from this theorem, the stationary energy distribution in such a system is specified, as soon as one knows the independent variables by which the state is determined.

**§ 166.** A comparison of the last formula with (242) shows, that we would be led by statistical mechanics to exactly the same connection among radiation density, temperature, and oscillation frequency [Schwingungszahl], as through the radiation law derived from the resonator vibrations, to be sure only for sufficiently long wavelengths, or else high temperatures. For only under these conditions is Equation (242) valid. From this restriction proceeds for the application of statistical mechanics to radiation processes a certain/definite [gewisse] difficulty. For if one would apply the theorem of equal energy distribution entirely unrestrictedly, then must that relationship hold entirely generally for all temperatures and frequencies, that that would, as one easily sees, result in the impossibility of a stationary energy distribution, since the energy density would along with [as a function of?—zugleich] the frequency increase without limit.

J. H. Jeans sought to remove this difficulty by the assumption, that in an with emitting and absorbing substance supplied radiating [durchstrahlten] cavity, no really stable radiation state exists, but on the contrary that the entire available energy in thermal radiation over time goes over to ever higher frequencies until eventually the velocity of

---

<sup>1</sup> See in addition A. Einstein, *Drudes Ann.* **17**, p., 132, 1905. The there emphasized difficulty standing against [?] radiation theory follows as a consequence that the condition (245) is there assumed at the outset as generally valid, while from the here developed theory the mentioned theorem of statistical mechanics only for sufficiently large values of the product  $\lambda T$  can claim validity. For details concerning this fundamentally important point see § 166.

<sup>2</sup> J. H. Jeans, *Phil. Mag.*, **10**, p. 91, 1905.

<sup>3</sup> Lord Rayleigh, *Nature* **72**, p. 54 and p. 273, 1905.

molecular motion has become imperceptibly small and the absolute temperature therefore equals zero.

To such an assumption I cannot however join myself. For if in every case? [ je] the theorem taken from everyday experience thereby gains in certainty, that the most diverse from it drawn consequences as with the most refined measurements in agreement are demonstrated, then it proves correct by the theorem, that the radiation in a with matter supplied cavity tends toward a final state with a definite final energy distribution between matter and aether. Up to now every in the theory of heat radiation described [?], to part from the first glance very bold appearing thermodynamic consequences, beginning from Kirchhoff's Law of the proportionality of emission power and absorbing power, is based on the assumption of the existence of in a thermodynamic sense an absolute equilibrium state, and everything would cut the ground from under it, if one drops this assumption; however, [dagegen] never has a consequence of this theorem been found in contradiction with experience. On the other side, has itself up to now [bisher] not the trace of an indication for it shown, which could lead to the conjecture, that in black radiation we do not have to do with a actual stable state, on the contrary: already the simple fact, that a body through thermal radiation can be warmed, that thus radiant energy can go over without compensation into energy of molecular motion, lets itself from that standpoint as well only with difficulty [nur schwer] be brought into agreement with the second law of thermodynamics.

I am therefore of the opinion that this difficulty has arisen only through an unjustified application of the theorem of equal energy distribution to all independent state variables. In fact for the justification of this theorem the assumption is essential, that the distribution of states for all possible systems with given total energy from the outset [von vornherein] is "ergodic",<sup>1</sup> or briefly expressed, that the probability, that the state of a system lies in a definite small "elementary domain" (§ 150), is simply proportional to the size of that domain, if the latter is taken as ever so small [*noch so klein*]. But this assumption is not satisfied by the stationary radiant energy; for the elementary domain cannot be taken arbitrarily small, on the contrary its size is finite, determined by the value of the elementary action quantum  $h$ . Only if one assumes that the action element  $h$  can be assumed infinitely small, would one arrive at the law of equal energy distribution. In fact for infinitely small  $h$ , as one sees from Formula (233), the general energy distribution goes over into the special here derived (269), and it is then valid in general all conditions of § 154, corresponding to the Rayleigh radiation law. For, corresponding to the theorem of equal energy distribution, the energy of all resonators would be equal to one another, something which in general is not the case.

Naturally the action element  $h$  must receive a direct electrodynamic meaning; but of what sort remains for the present an open question.

**§ 190. Conclusion.** The theory of irreversible radiation processes developed here explains why, in an irradiated cavity filled with oscillators of all possible frequencies, the radiation, regardless of its initial conditions, reaches a stationary state: the intensities and

---

<sup>1</sup> L. Boltzmann, Gastheorie II, p. 92, 101, 1898.



polarizations of all its components are simultaneously equilibrated in magnitude and direction. But the theory still is characterized by an essential gap. It treats only the interaction between radiation and oscillator vibrations at the same frequency. At a given frequency the continuous increase of entropy to a maximum value, required by the second law of thermodynamics, is therefore proven on purely electrodynamic grounds. But for all frequencies taken together the maximum reached in this way is not the absolute maximum of the system's entropy, and the corresponding state of the radiation is not in general the [state of] absolutely stable equilibrium (see § 27). The theory does not at all elucidate the manner in which the radiation intensities corresponding to different frequencies are simultaneously equilibrated, that is, the way in which the initial arbitrary distribution settles in time to the normal distribution characteristic of black radiation. The oscillators which proved the basis for the present treatment influence only the intensities of the radiation corresponding to their own natural frequencies. They are not able, however, to change its frequency if their effects are restricted to the emission and absorption of radiant energy.<sup>1</sup> (this paragraph is Kuhn's translation; check)

In order to obtain insight into those processes, through which in nature the exchange of energy between rays of different frequency is accomplished, requires it in any case also the investigation of the influence, which a motion of the oscillator exerts on the radiation process. For as soon as the oscillators move, comes it to collision between them, and with each collision must action come into play, which the vibrational energy of the oscillators still in entirely different and in more radical ways influences, than the simple emission and absorption of radiant energy. The end result of all these impact actions was foreseen [??] to be sure with the help of the probability considerations set up in the fourth chapter; but how in individual and in which period this result takes place, this to be taught is first the task of a future theory. Of such a theory are then undoubtedly also far reaching disclosures about the constitution of the in nature existing oscillators to be expected, because they in any case must also bring a closer explanation for the physical significance of the universal action element  $h$  (§ 149), which the electric elementary quantum certainly does not make way for [??] [nachsteht].

---

<sup>1</sup> See P. Ehrenfest, Wien. Ber. **114** [2a], p. 1301, 1905.