

under the conditions A and B. The simplest conclusion that might be drawn would be that these cases are not fundamentally different and that the limiting film transfer velocity in all cases depends, for a given surface,

- (1) on the temperature
- (2) on the minimum periphery in the connecting surface above the higher level.

The suggestion of Bowers and Mendelssohn that adsorbed air on the surface is responsible for anomalously high transfer rates would not appear inconsistent with this picture.

Finally, we are grateful to Dr. C. A. Reynolds and Mr. E. A. Lynton for their assistance with the experiment.

*Note added in proof.*—Professor F. Simon, at the recent Conference on Low Temperatures at M.I.T., has kindly drawn our attention to the fact that an estimate of the Type A film transfer rate may be computed from data given in reference (2). These measurements extend down to about 1.6°K and give a transfer rate of approximately  $8 \times 10^{-5}$  cm<sup>3</sup>/cm·sec. at this temperature, which is somewhat less than the value observed by us above.

## Collision Theories of Pressure Broadening of Spectral Lines

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It is shown that in the calculation of absorption in the Lorentz collision theory, it is essential to include the work done impulsively by the electric field during the sudden changes of position at collision. This work was implicitly included in the theory of Van Vleck and Weisskopf, but these authors did not give the breakdown into work done between and at collision. It is verified that the shapes of spectral lines for a classical harmonic oscillator and also a Debye slow rotator are the same in absorption and spontaneous emission, provided the energy density obeys the Rayleigh-Jeans law. The usual proofs of equilibrium simply establish equality of the integrated absorption and emission, without examining the detailed balancing at individual frequencies, not necessarily near resonance.

A COLLISION or impact theory of the width of spectral lines is one which conceives of the frequency distribution within a line as resulting from interruptions of the radiative process by collisions with molecules. The exact form of the resulting line width depends in a rather critical way on the detailed assumptions that are made about the nature of these interruptions, and there seems to be some confusion both as to concepts and terminology concerning the subject of impact broadening. The present paper attempts to clarify this situation.

### A. LORENTZ THEORY OF SPONTANEOUS RADIATION

As it is usually understood, the Lorentz<sup>1</sup> formula for line breadths results from simple Fourier analysis of a finite wave train radiated by a harmonically moving charge. Let the radiative frequency be  $\omega$ , and suppose that the radiation goes on for a time  $\theta$ . Then, if the amplitude is  $x_0$ , the Fourier analysis of the displacement

$$x(t) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} x(\omega') e^{i\omega' t} d\omega',$$

$$x(\omega') = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_0^{\theta} x_0 \cos(\omega\lambda + \phi) e^{-i\omega'\lambda} d\lambda.$$

When  $|x(\omega')|^2$  is averaged over a random distribution in the arbitrary phase constant  $\phi$ , the result is

$$|x(\omega')|^2 = \frac{x_0^2}{4\pi} \left[ \frac{1 - \cos(\omega' - \omega)\theta}{(\omega - \omega')^2} + \frac{1 - \cos(\omega' + \omega)\theta}{(\omega + \omega')^2} \right].$$

This expression must be integrated over all collision times  $\theta$  with a weighting function  $a e^{-a\theta}$ , where  $a$  is the mean collision frequency. One thus obtains

$$|x(\omega')|^2 = \frac{x_0^2}{4\pi} \left[ \frac{1}{a^2 + (\omega - \omega')^2} + \frac{1}{a^2 + (\omega + \omega')^2} \right].$$

According to classical mechanics, the power radiated by a charge  $e$  oscillating in one dimension is

\* Assisted by the ONR.

<sup>1</sup> H. A. Lorentz, Proc. Amst. Akad. Sci. 8, 591 (1906).

$\frac{2}{3}e^2c^{-3}(d^2x/dt^2)^2$ . Our Fourier components are normalized in such a way that

$$\int_{-\infty}^{\infty} x(t)^2 dt = \int_{-\infty}^{\infty} |x(\omega')|^2 d\omega' = 2 \int_0^{\infty} |x(\omega')|^2 d\omega'.$$

Hence the power emitted in the spectral interval  $\omega'$ ,  $\omega' + d\omega'$  is

$$P_E(\omega') d\omega' = (2e^2/3c^3) \cdot 2\omega'^4 |x(\omega')|^2 \cdot a \cdot d\omega'.$$

Here the factor  $a$  owes its origin to the fact that we have made the Fourier analysis of the displacement existing only in a single interval between two collisions, and in a very long time  $T$  there are  $aT$  such intervals. When we utilize our explicit formula for the mean square Fourier components, the expression for  $P_E(\omega')$  becomes

$$P_E(\omega') = \frac{e^2 x_0^2}{3\pi c^3} \omega'^4 \left[ \frac{a}{a^2 + (\omega - \omega')^2} + \frac{a}{a^2 + (\omega + \omega')^2} \right]. \quad (1)$$

### B. LINE SHAPE IN ABSORPTION

The shape of the spectral line can also be studied by examining absorption rather than spontaneous radiation. We calculate the power absorbed by an oscillating charge of natural frequency  $\omega$  from a light wave whose electric vector is  $E \cos(\omega't + \phi)$ . The oscillator is subject to collisions at times  $t_1, t_2, \dots$ , and each collision is supposed by Lorentz to have the effect of making  $x$  and  $\dot{x}$  zero abruptly at the instant of collision. The equation to be solved is then

$$\ddot{x} + \omega^2 x = (eE/m) \cos(\omega't + \phi),$$

and the solution wanted here is

$$x = \begin{cases} x_1 & \text{for } t_1 \leq t \leq t_2 \\ x_2 & \text{for } t_2 \leq t \leq t_3, \\ \text{etc.} \end{cases}$$

$$x_j = (eE/m\omega) \int_0^{t-t_j} \cos(\omega't - \omega'\lambda + \phi) \sin\omega\lambda d\lambda,$$

$$\dot{x}_j = (eE/m) \int_0^{t-t_j} \cos(\omega't - \omega'\lambda + \phi) \cos\omega\lambda d\lambda.$$

These integral forms, chosen to satisfy the conditions  $x_j(t_j) = \dot{x}_j(t_j) = 0$ , are most convenient in calculations.

The work done by the field is

$$W = \sum_j \int_{t_j}^{t_{j+1}} eE \cos(\omega't + \phi) \dot{x}_j dt. \quad (2)$$

When the substitution for  $\dot{x}_j$  is made and the difference

$t_{j+1} - t_j$  is replaced by  $\theta_j$  one obtains

$$W = (e^2 E^2 / m) \sum_j \int_0^{\theta_j} \cos(\omega't + \phi_j) \times dt \int_0^t \cos[\omega'(t-\lambda) + \phi_j] \cos\omega\lambda d\lambda, \quad (3)$$

with  $\phi_j = \omega't_j + \phi$ .

As to the distribution of collision times, we assume again that the number of intervals having duration between  $\theta$  and  $\theta + d\theta$  is  $ce^{-a\theta}d\theta$ , so that the total time of observation is

$$T = \int_0^{\infty} ce^{-a\theta} \theta d\theta = c/a^2.$$

Therefore, in Eq. (3),  $\sum_j$  may be replaced by

$$a^2 T \int e^{-a\theta} d\theta.$$

The presence of many absorbing atoms permits the assumption that the  $t_j$ , and hence the  $\phi_j$ , are distributed at random. The expression for  $W$  may then be simplified by averaging over  $\phi_j$  and it becomes

$$W = (e^2 E^2 / 2m) a T \int_0^{\infty} e^{-a\theta} d\theta \int_0^{\theta} dt \int_0^t \cos\omega'\lambda \cos\omega\lambda d\lambda. \quad (4)$$

At this stage it is well to remember the formula:

$$a \int_0^{\infty} e^{-a\theta} d\theta \int_0^{\theta} f(\lambda) d\lambda = \int_0^{\infty} e^{-a\lambda} f(\lambda) d\lambda.$$

On using it one obtains for the average power absorbed per atom

$$\frac{W}{T} = \frac{e^2 E^2}{4m} \left[ \frac{a}{a^2 + (\omega' - \omega)^2} + \frac{a}{a^2 + (\omega' + \omega)^2} \right]. \quad (5)$$

The so-called "structure" factor, which is enclosed by square brackets, and which determines the dependence on frequency near resonance, agrees with that in (1).

### C. CORRECTION OF LORENTZ FORMULA FOR WORK DONE DURING COLLISIONS

The preceding derivation, however, ignored the work done by the electromagnetic forces during collisions. As the oscillator displacement drops back from the value  $x_j(t_{j+1})$  to zero at the time  $t_{j+1}$ , its velocity is momentarily infinite. Because of this, there is added to the work given by Eq. (2) the increment

$$\lim_{\delta \rightarrow 0} \sum_j \int_{t_{j+1}-\delta}^{t_{j+1}+\delta} eE \cos(\omega't + \phi) \dot{x}_j dt.$$

A partial integration converts each term of this sum-

mation into

$$[eE \cos(\omega't + \phi)x]_{t_{j+1}-\delta}^{t_{j+1}+\delta} = -eE \cos(\omega't + \phi)x_j(t_{j+1}),$$

plus an integral which vanishes in the limit.

To the right-hand side of (3) one must then add

$$(-e^2E^2/m\omega)\sum_j \cos(\omega'\theta_j + \phi_j) \times \int_0^{\theta_j} \cos[\omega'(\theta_j - \lambda) + \phi_j] \sin\omega\lambda d\lambda.$$

If the same assumptions as before are made about the distribution of the  $\phi_j$  and  $\theta_j$ , Eq. (4) takes on an additional term

$$(-e^2E^2aT/2m\omega) \int_0^\infty e^{-a\theta} d\theta \int_0^\theta \cos\omega'\lambda \sin\omega\lambda d\lambda,$$

and  $W/T$ , previously given by Eq. (5), increases by

$$\frac{e^2E^2a}{4m\omega} \left[ \frac{\omega' - \omega}{a^2 + (\omega' - \omega)^2} - \frac{\omega' + \omega}{a^2 + (\omega' + \omega)^2} \right]. \quad (6)$$

This is the power spent against the forces during collisions. In the optical range of frequencies, where  $\omega$  and  $\omega'$  are nearly equal and both are very large, (6) is negligible in comparison with (5). It may also be noted that the power spent during collisions is abstracted from the light wave on one side of the spectral line, delivered to it on the other. When (5) and (6) are combined, the result is

$$(W/T) = \frac{e^2E^2\omega'}{4m\omega} \left[ \frac{a}{a^2 + (\omega' - \omega)^2} - \frac{a}{a^2 + (\omega' + \omega)^2} \right]. \quad (7)$$

Van Vleck and Weisskopf<sup>2</sup> have derived Eq. (7) directly by computing the *mean* displacement of all oscillators and then differentiating it with respect to time to obtain the mean velocity. The work done at collisions is implicitly taken into account because the discontinuities at collision affect the time derivative of the mean displacement at any given instant even though they do not enter in the mean velocity of a particle between collisions. The significance of the procedure of Van Vleck and Weisskopf is made more explicit and clearer by the method of the present paper, which segregates the contributions of the work done between and at collisions, and which is therefore perhaps not entirely without interest. Van Vleck and Weisskopf call (7) the Lorentz formula. To what expression one attributes this name is to a large extent a matter of personal choice and opinion, as the calculations of Lorentz are many-sided. It is probably more customary to approach the problem of spectral distribution from the standpoint of spontaneous radiation

rather than absorption; then one is led to regard (1) rather than (7) as the Lorentz formula.

As the structure factor is different in (1) and (7), it would at this stage appear that the shapes of emission and absorption lines are different, in violation of the thermodynamics of radiation. This dilemma, however, is removed when allowance is made for the fact that after collision the displacements should be taken as distributed according to the Boltzmann law rather than random, as Lorentz supposed. Van Vleck and Weisskopf show that a further contribution to  $W/T$  must be included if it is assumed that, after collision, an oscillator does not snap back to a zero (or mean zero) displacement, but to the value

$$(eE/m\omega^2) \cos\phi_j,$$

which is the mean of the displacement of all oscillators, computed with the Boltzmann weighting factor, in the field of the light wave at  $t_j$ . This requires a further addition to the power given by Eq. (7) of amount

$$\frac{e^2E^2a}{4m\omega^2} \left[ \frac{\omega'^2 - \omega'\omega}{a^2 + (\omega' - \omega)^2} + \frac{\omega'^2 + \omega'\omega}{a^2 + (\omega' + \omega)^2} \right]. \quad (8)$$

(Van Vleck and Weisskopf do not give the breakdown of (8) in terms of work done between and at collisions; a simple calculation by the methods of the present paper shows that the contribution of the former to (8) just equals the expression (6) in value, and that the balance of (8) is accounted for by the impulsive work at collision.)

#### D. BALANCE BETWEEN EMISSION AND ABSORPTION

Formulas (7) and (8) relate to power absorbed from a monochromatic wave of amplitude  $E$  and frequency  $\omega'$ . To study the spectral distribution of the absorption in a non-monochromatic radiation field, we must replace  $E^2$  by  $8\pi\rho(\omega')d\omega'/3$  and make some assumption concerning how the energy density  $\rho(\omega')$  of radiation varies with frequency. When we make this replacement and add (8) to (7), we find that the energy absorbed in the interval  $\omega', \omega' + d\omega'$  is  $P_A(\omega')d\omega'$  with

$$P_A(\omega') = \frac{2\pi e^2\omega'^2}{3m\omega^2} \left[ \frac{a}{a^2 + (\omega' - \omega)^2} + \frac{a}{a^2 + (\omega' + \omega)^2} \right] \rho(\omega'). \quad (9)$$

Since our calculation is purely classical, we should expect equilibrium between absorption and spontaneous emission if the energy density has the Rayleigh-Jeans value

$$\rho(\omega') = kT\omega'^2/\pi^2c^3. \quad (10)$$

Indeed, the expression (9) just equals (1) if we use (10) and also employ, as we should, in (1) the equipartition value  $x_0^2 = 2kT/m\omega^2$  for the statistical average of the square of the amplitude of a harmonic oscillator.

The literature is full of proofs that the total integrated

<sup>2</sup> J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. 17, 227 (1947).

absorption and emission of a harmonic oscillator balance in a Rayleigh-Jeans radiation field. However, so far as we know, no explicit verification has previously been published that the shapes of the absorption and emission lines are the same.

It should be noted that our proof of the equilibrium required utilization of the correction (8) introduced by Van Vleck and Weisskopf to allow for the fact that after collisions the phases are distributed in accordance with the Boltzman law. Without this correction, balance between absorption and emission is not secured. It is true because of Eq. (5) that if one neglects the impulsive work done at collisions and assumes random phasing after collision, the absorbed energy will differ from the emitted only by a factor  $\omega^2/\omega'^2$ ,—a distinction unimportant in the immediate vicinity of resonance, the case usually considered. Exact compensation at all frequencies is required, however, if detailed balancing is to hold. Accurate fulfillment of this requirement can be regarded as additional confirmation of the correctness of the Van Vleck-Weisskopf shape factor for absorption.

It should also be mentioned that in the calculation of spontaneous emission at the beginning of this paper, we implicitly took into account the sudden changes of position at collision, with attendant singularities in velocity and acceleration. For we made a Fourier analysis of the displacement, and multiplied by  $-\omega'^2$  to obtain the Fourier components of the acceleration. If instead we made directly the Fourier analysis of an acceleration which is  $-x_0\omega^2 \cos(\omega t + \phi)$  over a time interval  $\theta$ , and zero elsewhere, thus neglecting the infinite accelerations at collision, the Fourier components of the acceleration would differ by a factor  $\omega^2/\omega'^2$  from those we use. Then a factor  $\omega^4/\omega'^4$  would be introduced in (1), and the balance between emission and absorption spoiled.

### E. THE SLOW ROTATOR

The need of considering the spontaneous radiation arising from the impulsive changes in position at collision becomes particularly clear if one utilizes the model employed by Debye<sup>3</sup> in studying absorption and dispersion at radiofrequencies in liquids. He takes the

<sup>3</sup> P. Debye, *Polar Molecules* (The Chemical Catalog Company, Inc., New York, 1929), Chapter V. For the calculation of the absorption with the Lorentz model of strong collisions, see especially Van Vleck and Weisskopf, reference 2.

molecular system to be a rigid dumb-bell whose proper frequency of rotation is small compared with the collision parameter  $a$ . Except for vibrations forced by the applied field, the molecule thus is regarded as standing still between collisions. Hence no spontaneous radiation at all would be obtained if one tried to apply the Fourier analysis only to the acceleration for the interval between collisions. On the other hand, emission of the proper amount is obtained if (1) is used. In this connection, the proper frequency  $\omega$  is to be taken as zero and the quantity  $e^2x_0^2$  in (1) is to be replaced by  $2\mu^2$  inasmuch as the circular rotation of a dipole of moment  $\mu$  can be resolved into two simple harmonic motions of amplitude  $\mu$  in two orthogonal directions. Various authors have shown that the absorption by the slow rotator is given by

$$P_A(\omega') = \frac{4\pi\mu^2\omega'^2}{3kT} \frac{a}{\omega'^2 + a^2} \rho(\omega'). \quad (11)$$

There is exact agreement between (11) and (1) (with  $\omega=0$ ,  $e^2x_0^2=2\mu^2$ ) when the energy density has the Rayleigh-Jeans form (10).

In closing we should like to emphasize that the calculations of the present paper are based entirely on the Lorentz model of infinitely short collisions with no persistence in phase. For actual atomic systems, corrections for the finite length of collision may alter the line shape. Also, in quantum mechanics, where the Planck radiation law replaces that of Rayleigh-Jeans, the problem of the calculation of the shape of the absorption curve and verification of detailed balancing is far more difficult than in classical theory; we have not succeeded in solving it accurately even for collisions of the Lorentz type. In the microwave region, however, there is no difficulty, as  $\omega'$  is small compared with  $kT/h$ , and the Planck formula reduces to that of Rayleigh-Jeans. In this region, the shape factor is therefore appropriately given by (1) or (9) for the Lorentz model of collisions even if quantum mechanics is used. In particular, a quantum-mechanical derivation of the Van Vleck-Weisskopf absorption formula has been given by Karplus and Schwinger.<sup>4</sup>

We wish to thank Professor D. M. Dennison for calling our attention to the desirability of studying line shapes simultaneously in absorption and emission.

<sup>4</sup> R. Karplus and J. Schwinger, *Phys. Rev.* **73**, 1020 (1948).