and according to the first equation of [58]

$$E = \frac{CW}{\theta_1} D_1{}^* e^{-(t/\theta_1)} + \frac{CW}{\theta_2} D_2{}^* e^{-(t/\theta_2)}.$$

The other three quantities, I, F and X, can likewise be expressed with the help of $D_1{}^*$ and $D_2{}^*$, using the three remaining equations. So, for instance, we will find

$$\begin{aligned} 3p_1X = &\left[(1 - p_0) - \frac{CW}{\theta_1}(1 + 2p_0) \right] D_1{}^* e^{-(t/\theta_1)} \\ &+ \left[(1 - p_0) - \frac{CW}{\theta_2}(1 + 2p_0) \right] D_2{}^* e^{-(t/\theta_2)}. \end{aligned} \qquad [60']$$

Now we have two conditions at the beginning $t = 0$ of the experiments. First we know the total charge on one plate of the condenser, or, in other words, we know the initial dielectric displacement, which we will call D_0. Secondly, we know that for $t = 0$ the distribution of the moments is given by Boltzmann's function. Calling F_0 the initial internal force, we know, therefore, that for $t = 0$ we have the condition $X(0) = F_0$. But in the statical case F_0 is found with the help of Mosotti's assumption to be equal to $[(\epsilon+2)/3\epsilon]D_0$ in a medium with the dielectric constant ϵ. Our second condition therefore has (for $t = 0$) the form

$$X(0) = \left[1 + 2\frac{1 - (p_0 + p_1)}{1 + 2(p_0 + p_1)} \right] \frac{D_0}{3} = \frac{D_0}{1 + 2(p_0 + p_1)}.$$

Using both initial conditions, the two constants $D_1{}^*$ and $D_2{}^*$ can be expressed in terms of the initial displacement D_0. The final result for D is

$$\begin{aligned} \left(\frac{CW}{\theta_1} - \frac{CW}{\theta_2} \right) \frac{D}{D_0} = &\left(\frac{CW}{\theta_1} e^{-(t/\theta_2)} - \frac{CW}{\theta_2} e^{-(t/\theta_1)} \right) \\ &- \frac{1}{\epsilon}\left(e^{-(t/\theta_2)} - e^{-(t/\theta_1)} \right), \end{aligned} \qquad [61]$$

showing that in general the time function is a superposition of two exponentials. A special case of some interest is obtained if the resistance W is taken so small that the usual time of discharge would be small compared with the relaxation time of the dielectric. From [59] it is found in the limit for $W = 0$ that

$$\frac{1}{\theta_1} = \frac{1 - p_0}{1 + 2p_0} \frac{1}{CW}, \qquad \frac{1}{\theta_2} = \frac{1 - p_0 - p_1}{1 - p_0} \frac{1}{\tau};$$

substituting these values in [61] yields

$$\frac{D}{D_0} = \frac{\epsilon_0}{\epsilon} e^{-(t/\epsilon_0 CW)} + \left(1 - \frac{\epsilon_0}{\epsilon} \right) e^{-(1-p_0-p_1)/(1-p_0)(\tau/t)}, \qquad [61']$$

where we have used the notation

$$\frac{1 + 2p_0}{1 - p_0} = \epsilon_0,$$

since this would be the dielectric constant if the molecules were non-polar ($\mu = 0$). Equation [61′] shows how a first part of the dielectric displacement $(\epsilon_0/\epsilon)D_0$, and therefore of the charge too, vanishes in a time comparable with $\epsilon_0 CW$, which is supposed to be a very short time. It is the time of discharge of a condenser filled with a fictitious substance whose dielectric constant would be determined by the distortion alone. The remaining part $[1 - (\epsilon_0/\epsilon)]D_0$ vanishes in a time comparable with $[(1-p_0)/(1-p_0-p_1)]\tau$, which can be several times the characteristic relaxation time τ if $p_0 + p_1$ is not very different from 1. This is to be expected for substances with a high dielectric constant, according to the formula

$$\epsilon = \frac{1 + 2(p_0 + p_1)}{1 - (p_0 + p_1)},$$

which will give large values of ϵ if the denominator does not differ greatly from zero.

18. Polar Liquids under the Influence of High Frequencies.

Practically much more important than the case treated in the foregoing Section 17 are the dielectric properties in a periodic field. Let the number of vibrations in 2π seconds be ω; the internal force may then be expressed by the real part of

$$F = F_0 e^{i\omega t},$$

so that the torque on a molecule is given by

$$M = -\mu F_0 e^{i\omega t} \sin \vartheta.$$

As in the previous case the distribution function must be a solution of [48], which we can write in the form

$$2\tau \frac{\partial f}{\partial t} = \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left[\sin \vartheta \left(\frac{\partial f}{\partial \vartheta} - \frac{fM}{kT} \right) \right].$$

Let us try as a solution

$$f = A \left[1 + B \frac{\mu F_0}{kT} e^{i\omega t} \cos \vartheta \right],$$

where B is a constant as yet arbitrary. The substitution of this expression in [48] shows that the differential equation is satisfied, providing we choose B complex according to the equation[5]

$$B = \frac{1}{1+i\omega\tau}.$$

We have then

$$f = A\left[1+\frac{1}{1+i\omega\tau}\frac{\mu F}{kT}\cos\vartheta\right]. \qquad [62]$$

For $\omega = 0$ we have the usual Maxwell-Boltzmann function, while for very large values of $\omega\tau$ the function becomes constant. The transition from one case to the other occurs for frequencies which will make $\omega\tau$ of order of magnitude unity. The mean moment of the molecules is also complex and is given by the equation

$$\overline{m} = \frac{\mu^2}{3kT}\frac{F}{1+i\omega\tau} = \frac{\mu^2}{3kT}\frac{F_0 e^{i\omega t}}{1+i\omega\tau}. \qquad [63]$$

The meaning of the complex moment is of course that there is a difference in phase between the moment and the internal force. If the phase angle is φ, the above equation may be written in the form

$$\overline{m} = \frac{\mu^2}{3kT}\frac{F_0}{\sqrt{1+\omega^2\tau^2}}e^{i(\omega t-\varphi)},$$

where

$$\tan\varphi = \omega\tau.$$

Now it is well known that a difference in phase between field intensity and polarization is always accompanied by energy absorption. As a result of the existence of a finite relaxation time, we will therefore not only encounter dispersion but also absorption intimately connected with it.[6] We are going to consider these phenomena in some detail, assuming Mosotti's hypothesis to hold.

The molar polarization P in this case is expressed by

$$\frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho} = P(\omega) = \frac{4\pi N}{3}\left[\alpha_0+\frac{\mu^2}{3kT}\frac{1}{1+i\omega\tau}\right], \qquad [64]$$

which is complex and a function of the frequency. Solving this

---

[5] Quantities of higher than the first order in F are again neglected.

[6] As another consequence of the existence of such a difference in phase it is known that in a rotating electric field of constant intensity a dielectric will begin to rotate. The reason why the phase difference exists does not matter at all; any dielectric showing conductivity or dielectric losses will exhibit the effect. [*Compare* A. Winkelmann, "Handbuch der Physik," IV, 1, p. 161, and G. Breit, *Z. Physik*, **11**, 129 (1922).] M. Born, *Z. Physik*, **1**, 221 (1920), starting from another point of view, calculated the torque on a polar liquid, whose absorption is due to the relaxation effect mentioned in the text. (*Compare also* P. Debye, "Handbuch der Radiologie," V, p. 652.) Successful experiments were carried out by P. Lertes, *Z. Physik*, 4, 56 (1921).

equation for ϵ, we find

$$\epsilon = \frac{1+2\frac{\rho}{M}P(\omega)}{1-\frac{\rho}{M}P(\omega)}. \qquad [64']$$

Instead of characterizing the liquid by the two theoretical constants α_0 and $\mu^2/3kT$ it is advisable to use the two dielectric constants ϵ_0 and ϵ_1 defined by

$$\left.\begin{aligned}\frac{\epsilon_0-1}{\epsilon_0+2}\frac{M}{\rho} &= \frac{4\pi}{3}N\alpha_0,\\ \frac{\epsilon_1-1}{\epsilon_1+2}\frac{M}{\rho} &= \frac{4\pi}{3}N\left(\alpha_0+\frac{\mu^2}{3kT}\right).\end{aligned}\right\} \qquad [65]$$

According to [64] the dielectric constant ϵ_0 will then denote the value of ϵ for high frequencies, the optical dielectric constant, as we will call it, and ϵ_1 will be the statical dielectric constant, observed for $\omega = 0$. With these definitions the molar polarization takes the form

$$P(\omega) = \frac{M}{\rho}\left[\frac{\epsilon_0-1}{\epsilon_0+2}+\frac{1}{1+i\omega\tau}\left(\frac{\epsilon_1-1}{\epsilon_1+2}-\frac{\epsilon_0-1}{\epsilon_0+2}\right)\right]$$

and we obtain for the dielectric constant as a function of ω the expression

$$\epsilon = \frac{\dfrac{\epsilon_1}{\epsilon_1+2}+i\omega\tau\dfrac{\epsilon_0}{\epsilon_0+2}}{\dfrac{1}{\epsilon_1+2}+i\omega\tau\dfrac{1}{\epsilon_0+2}}. \qquad [66]$$

According to the formal theory of propagation of light ϵ is equal to the square of the generalized refraction index, but as ϵ is here an imaginary quantity, the generalized refraction index will also have an imaginary part. In the usual way we therefore put

$$\epsilon = r^2(1-i\kappa)^2 \qquad [66']$$

such that r and κ are both real quantities, r being the ordinary refraction index and κ the absorption index.

The meaning of the two constituents of the generalized refractive index is seen, if it is remembered that the field intensity of a plane wave travelling in the s-direction is proportional to the expression

$$e^{i\omega\left[t-\frac{r(1-i\kappa)}{c}s\right]} = e^{-\omega\kappa\frac{r}{c}s}\,e^{i\omega\left[t-\frac{r}{c}s\right]},$$

if we denote by c the velocity of light in vacuum. If the wave-length in vacuum is λ_0, the wave-length in the medium is $\lambda = \lambda_0/r$ and the amplitude is multiplied by $e^{-2\pi\kappa}$ after the wave has travelled over a distance of one wave-length λ.

In order to discuss the refraction index r and the absorption index κ as functions of the frequency, we introduce the variable

$$x = \frac{\epsilon_1 + 2}{\epsilon_0 + 2}\omega\tau. \qquad [67]$$

It can then be shown that [66] is equivalent to the two equations

$$\left.\begin{aligned} r^2 &= \frac{1}{2}\left[\sqrt{\frac{\epsilon_1^2 + \epsilon_0^2 x^2}{1 + x^2}} + \frac{\epsilon_1 + \epsilon_0 x^2}{1 + x^2}\right], \\ r^2\kappa^2 &= \frac{1}{2}\left[\sqrt{\frac{\epsilon_1^2 + \epsilon_0^2 x^2}{1 + x^2}} - \frac{\epsilon_1 + \epsilon_0 x^2}{1 + x^2}\right], \end{aligned}\right\} \qquad [68]$$

giving values for r and for $r\kappa$ separately.

Calling $\epsilon_0/\epsilon_1 = p$, equation [66] can be written in the form

$$\frac{\epsilon}{\epsilon_1} = \frac{1 + ipx}{1 + ix}.$$

If now two angles φ and ψ are introduced by the equations $\tan\varphi = x$ and $\tan\psi = px$, it can be shown that

$$\frac{r^2}{\epsilon_1} = \frac{\cos\varphi}{\cos\psi}\cos^2\left(\frac{\varphi - \psi}{2}\right) = \frac{1}{2}\frac{\cos\varphi}{\cos\psi}\{1 + \cos(\varphi - \psi)\},$$

$$\frac{r^2\kappa^2}{\epsilon_1} = \frac{\cos\varphi}{\cos\psi}\sin^2\left(\frac{\varphi - \psi}{2}\right) = \frac{1}{2}\frac{\cos\varphi}{\cos\psi}\{1 - \cos(\varphi - \psi)\}.$$

These equations can easily be transformed into the functions of [68], remembering the definition of φ and ψ. The introduction of these angles is of some help in deriving additional results below in the text, which are given without proof.

In the interval $x = 0, \cdots x = \infty$, the square of the refractive index ranges from $r^2 = \epsilon_1, \cdots r^2 = \epsilon_0$; the product $r^2\kappa^2$ starts with 0 for $x = 0$, goes through a maximum and comes back to 0 again for $x = \infty$, and the same is true for the absorption index κ alone. Figure 26 shows this behavior in a special case. Some details may be of interest, from the standpoint of the description of an actual experiment.

The absorption index κ has a maximum for the frequency ω given by the formula

$$\omega\tau = \frac{\epsilon_0 + 2}{\epsilon_1 + 2}\sqrt{\frac{\epsilon_1}{\epsilon_0}}.$$

This maximum value itself is

$$\kappa_{\text{max.}} = \frac{\sqrt{\epsilon_1} - \sqrt{\epsilon_0}}{\sqrt{\epsilon_1} + \sqrt{\epsilon_0}}$$

and at the corresponding frequency the square of the refraction index is given as

$$r^2 = \frac{1}{2}\frac{\sqrt{\epsilon_0\epsilon_1}}{\epsilon_0 + \epsilon_1}(\sqrt{\epsilon_0} + \sqrt{\epsilon_1})^2.$$

In the special case of decidedly polar molecules for which ϵ_1 is large compared with ϵ_0, the frequency at which the maximum of κ occurs will be appreciably smaller than the characteristic frequency $1/\tau$ and the maximum value itself will be nearly equal to unity.

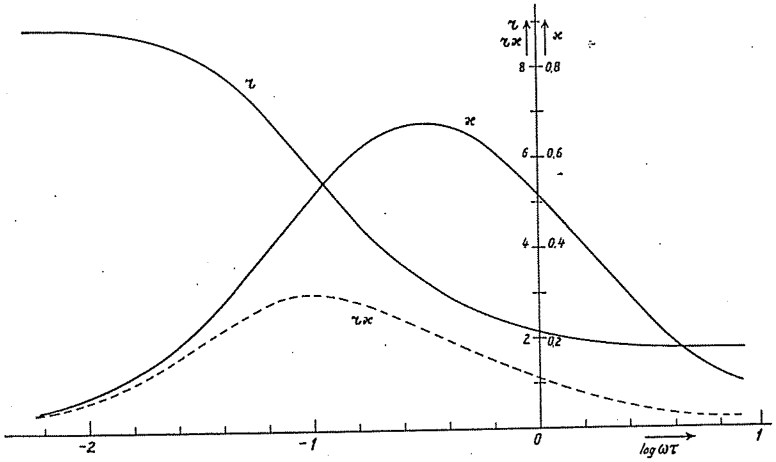

FIG. 26. Dispersion and absorption in polar liquids.

A distance of one wave-length (measured in the medium) is then sufficient to decrease the amplitude to $\epsilon^{-2\pi} = 1.85 \times 10^{-3}$ of its initial value. At this place in the spectrum the square of the refraction index is under the same conditions approximately equal to $\frac{1}{2}\sqrt{\epsilon_0\epsilon_1}$.

The product $r\kappa$ is the significant quantity in estimating the absorption if the range is measured in terms of the wave-length λ_0 measured in vacuum, for the amplitude of a wave after travelling over the distance s is proportional to $e^{-2\pi\kappa r(s/\lambda_0)}$. This product reaches its maximum value ~~at~~ a frequency different from that which makes κ a maximum; namely, if

$$\omega\tau = \frac{\epsilon_0 + 2}{\epsilon_1 + 2}\sqrt{\frac{3\epsilon_1 + \epsilon_0}{\epsilon_1 + 3\epsilon_0}},$$

and the maximum value is given by the expression

$$(r\kappa)_{\text{max.}} = \frac{\epsilon_1 - \epsilon_0}{2\sqrt{2(\epsilon_1 + \epsilon_0)}}.$$

At this place in the spectrum the square of the refractive index is

$$r^2 = \frac{(3\epsilon_1 + \epsilon_0)(\epsilon_1 + 3\epsilon_0)}{8(\epsilon_1 + \epsilon_0)},$$

which is nearly equal to $\frac{3}{8}\epsilon_1$, if $\epsilon_1 \gg \epsilon_0$.

To estimate the relaxation time τ from the experimentally obtained dispersion-curve for r_2 it is convenient to note that the square of the refraction index will be midway in its change from ϵ_1 to ϵ_0 (*i.e.*, will have acquired the value $(\epsilon_1 + \epsilon_0)/2$) if $\omega\tau$ is equal to

$$\omega\tau = \frac{\epsilon_0 + 2}{\epsilon_1 + 2}\sqrt{\frac{1}{2}\left[\frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + \epsilon_0} + \sqrt{4 + \left(\frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + \epsilon_0}\right)^2}\right]}\,.$$

In the special case that again $\epsilon_1 \gg \epsilon_0$, this equation yields

$$\frac{\epsilon_1 + 2}{\epsilon_0 + 2}\omega\tau = \sqrt{\frac{1 + \sqrt{5}}{2}} = 1.27.$$

The result of actual experiments on the absorption, measured for instance with a bridge method, is frequently given in terms of a phase angle Φ. If the potential difference between the plates of the condenser is $Ve^{i\omega t}$ and the dielectric constant ϵ has to be decomposed into a real part and an imaginary part

$$\epsilon = \epsilon' - i\epsilon'',$$

the charge Q on one of the plates (omitting constant factors) will be

$$Q = (\epsilon' - i\epsilon'')Ve^{i\omega t}.$$

The phase angle can then be defined by the equation

$$\tan\Phi = \frac{\epsilon''}{\epsilon'}\,.$$

Going back to equations [66] and [67], it is easily seen that

$$\epsilon' = \epsilon_0 + \frac{\epsilon_1 - \epsilon_0}{1 + x^2},$$

$$\epsilon'' = \frac{(\epsilon_1 - \epsilon_0)}{1 + x^2}x,$$

and therefore

$$\tan\Phi = \frac{(\epsilon_1 - \epsilon_0)x}{\epsilon_1 + \epsilon_0 x^2}\,.$$

This phase angle reaches a maximum value at the same place in the spectrum where the absorption index κ is a maximum ($x^2 = \epsilon_1/\epsilon_0$) and can be calculated at this place from the equation

$$\tan\Phi_{\text{max.}} = \frac{1}{2}\frac{\epsilon_1 - \epsilon_0}{\sqrt{\epsilon_1\epsilon_0}}\,.$$

At this frequency, for which $\kappa = \kappa_{\text{max.}}$, the two parts of ϵ are

$$\epsilon' = 2\frac{\epsilon_1\epsilon_0}{\epsilon_1 + \epsilon_0} \qquad \text{and} \qquad \epsilon'' = \frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + \epsilon_0}\sqrt{\epsilon_1\epsilon_0}.$$

19. Experiments on the Anomalous Dispersion and Absorption of Polar Liquids.

The weakest point in the theory presented in the foregoing Section 18 is the introduction of Mosotti's hypothesis, if the results are to be compared with actually existing experiments. These experiments have been performed with decidedly polar liquids. Now we know that these liquids always show association and it is very doubtful, indeed improbable, that we can make Mosotti's assumption about the internal field. We therefore should expect that the results of the actual experiments will deviate from the formula calculated for the ideal liquid treated in Section 18, although only in a quantitative and not in a qualitative way. However, if future experiments are made on dispersion, using sufficiently diluted solutions of polar molecules in non-polar liquids like benzene or hexane, we will then have a perfect right to apply the formulas to this case. Moreover it would be interesting from a purely experimental point of view to see how the characteristic region of anomalous dispersion shifts to longer wave-lengths, as we expect it to do, if the inner friction of the non-polar *solvent* is changed by lowering the temperature, or, for instance, by using a series of non-polar saturated hydrocarbons with increasing viscosities.

It is with these restrictions in mind that we are going to discuss some recent experiments of Mizushima,[7] which seem to be best to the point. Many former experiments of other investigators have given indications in the same direction, but are less complete.[8] According to our exposition the only new quantity entering in the equations for the description of anomalous dispersion and absorption was the product of the relaxation time τ and the frequency ω, as is seen, for instance, in equation [66]. This means that for these phenomena a correspondence law should hold stating that any effect of the frequency can likewise be obtained at constant frequency by

[7] San-ichiro Mizushima, *Bull. Chem. Soc. Japan*, **1**, 47, 83, 115, 143, 163 (1926); *Physik. Z.*, **28**, 418 (1927).

[8] O. v. Baeyer, *Ann. Physik*, **17**, 30 (1905); F. Eckert, *Verhandl. deut. physik. Ges.*, **15**, 307 (1913); H. Rubens, *ibid.*, **17**, 335 (1915); E. F. Nicholls and J. D. Tear, *Phys. Rev.*, **21**, 587 (1923); J. D. Tear, *Phys. Rev.*, **21**, 600 (1923); R. Bock, *Z. Physik*, **31**, 534 (1925).