state of the molecule and not as an average of all states. Impurities are no longer of importance since the spectrum of a specific molecule is examined. Microwave measurements on Stark effects are made at gas pressure of only about 0.01 mm Hg, hence many substances can be studied in the vapor state without danger of association. Accuracies to 0.01 debye can be obtained,[14] while a measurement of the dipole moment from the temperature dependence of the dielectric constant (see Sec. 16) is, in general, not more accurate than 0.1 debye. Stark effect measurements on the NH_3 inversion spectrum have led to the permanent moment $\mu = 1.45$ [debye].[15]

This superior accuracy of microwave spectroscopy, however, does not imply that direct electric measurements of dipole moments have become unnecessary. The Stark effect technique is applicable only for simple molecules where the theory can be worked out. Furthermore, it does not extend to the liquid and solid phases, where the resonance spectra of rotation have been destroyed (see Secs. 22 ff.).

Microwave measurements, finally, allow a detailed study of the pressure broadening of spectral lines. As a first result of observations, as in Fig. 21.6, a comparison is obtained between the gaskinetic collision time τ_c (see Eq. 20.21) and the actual average time interval between collisions. This time proves to be about fifteen times shorter than the kinetic theory predicts; obviously, the large dipole moment of the ammonia molecule has increased its collision radius appreciably. At higher pressures the collision damping becomes so strong that not a symmetrical but an asymmetrical broadening of the line results. The resonance peak shifts to lower frequencies[16] as already foreseen by the simple oscillator theory (see Eq. 4.9).

Microwave spectral lines like the 3,3 line of ammonia at 23,870 megacycles are under consideration as primary frequency standards and for the control of "atomic clocks" which might compare atomic time with sidereal time.[17] Our present frequency standards are based on "quartz clocks" operating by piezoelectric resonance (see Sec. 26).

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[14] See, for example, R. G. Shulmann, B. P. Daily, and C. H. Townes, *Phys. Rev. 78*, 145 (1950).

[15] See P. Kisliuk and C. H. Townes, Molecular Microwave Spectra Tables, *J. Res. U. S. Natl. Bur. Stand. 44*, 611 (1950).

[16] B. Bleany and J. H. N. Loubser, *Proc. Phys. Soc. (London)* A*63*, 483 (1950).

[17] H. Lyons, *Phys. Rev. 74*, 1203 (1948); *Ann. N. Y. Acad. Sci. 55*, 831 (1952).

22 · Pressure Broadening and Debye's Relaxation Equation

In discussing the frequency dependence of the permittivity of gases, we started with the anomalous dispersion and resonance absorption of linear harmonic oscillators (see Sec. 4). The dispersion formula of classical physics thus derived predicted correctly the general shape of spectral lines. It was impossible, however, to foresee the intensity and frequency location of these lines from classical considerations because the existence of stationary energy states of atoms and molecules is a nonclassical phenomenon. Only by passing from Newtonian mechanics to quantum mechanics was an interpretation obtained of the stationary states of electronic excitation, vibration, and rotation as standing-wave patterns of the probability waves, and of the spectral lines as transitions between the various energy levels. The intensity of the lines proved to be given by the statistical weight of the terms (their multiplet structure) and by the transition probabilities (see Secs. 12 and 19). The line width results from radiation damping, Doppler effect, and collision broadening (see Sec. 20); for higher pressures, collision damping becomes the decisive factor. Since the density of the condensed phases corresponds to that of normal gases under several thousand atmospheres of pressure, the pressure broadening of spectral lines has to be considered as one important aspect in the discussion of the dielectric absorption of solids and liquids.

That a rapid sequence of interrupting collisions will make the formation of discrete quantum states impossible can be derived immediately from the uncertainty relation (Eq. 8.11):

$$\Delta\mathcal{E}\, \Delta t \geq \hbar. \tag{22.1}$$

If the time interval Δt equals the natural life span τ of the quantum state (Δt = maximum), the energy state $\mathcal{E}$ is defined with optimum sharpness ($\Delta\mathcal{E}$ = minimum). If, on the other hand, a disrupting collision takes place during every vibration or rotation cycle ($\Delta t = 1/\nu$), the uncertainty in the definition of the energy state becomes

$$\Delta\mathcal{E} = \hbar\nu, \tag{22.2}$$

that is, of the order of magnitude of the total quantum energy. The resonance state in this case has vanished, and the spectral line has broadened into a continuum; the resonator, classically speaking, has been overdamped.

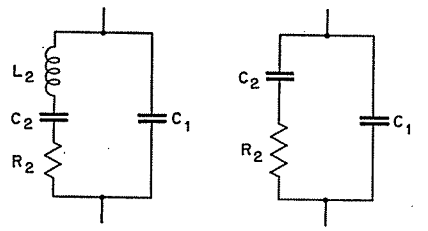
In Sec. 20 we treated the case of pressure broadening by substituting in the damping factor of Eq. 4.14

$$2\alpha = 1/\tau, \tag{22.3}$$

the time interval τ_c between collisions in place of the natural lifetime τ of the quantum state. This seems justified if many *weak collisions* constitute a continuous drain on the energy of the oscillator without causing abrupt changes in amplitude and phase. In contrast, the pool game of gas kinetics visualizes frequently the interaction of molecules as a statistical sequence of *strong collisions*, each of them altering the energy and momentum of the partners violently. Under such conditions, the amplitude and phase of the classical oscillator varies discontinuously, and not the steady-state solution (Eq. 4.27) of the force equation applies but the general solution composed of steady-state and transient terms.

The dispersion formula of classical physics pictures, electrically speaking, the resonating atoms or molecules in the gaseous state as L, R, C circuits shunted by a capacitance (*a*). The classical approach to the treatment of dipole molecules in the condensed phases of liquids and solids is to consider the polar molecules as rotating in a medium of dominating friction.[1] We postulate, in effect, that the acceleration term can be neglected, that is, that the L, R, C equivalent circuit reduces to an R, C circuit (*b*), (Fig. 22.1). In this extreme case of weak-collision broadening we thus substitute by hunch for the resonance spectrum of Fig. 4.2 the relaxation spectrum of I, Fig. 26.5, with its complex permittivity (see I, Eq. 26.14),

$$\kappa^* = \kappa_\infty' + \frac{\kappa_s' - \kappa_\infty'}{1 + j\omega\tau}. \tag{22.4}$$



(a) Resonator (b) Rotator in medium where friction term dominates

Fig. 22.1. Equivalent circuits of free resonator molecule and of rotator molecule in medium of dominating friction.

Now only the task remains to reinterpret the static and optical permittivities κ_s' and κ_∞', and the relaxation time τ by molecular quantities.

The optical dielectric constant κ_∞', represented in the electric circuit analogue by the by-pass capacitor, contains the contribution of the induced moments

$$\boldsymbol{\mu}_i = (\alpha_e + \alpha_a)\mathbf{E}' \tag{22.5}$$

caused by the electronic and atomic polarizabilities of the molecules (the deformation polarization). The static dielectric constant κ_s' contains, in addition, the orientation polarization of the permanent moments $\boldsymbol{\mu}$. According to the statistical theory of Sec. 16, when the electric field energy is small in comparison to the thermal energy of agitation, each dipole molecule contributes an average moment (see Eq. 16.9)

$$\bar{\boldsymbol{\mu}}_d = \frac{\mu^2}{3kT}\mathbf{E}'. \tag{22.6}$$

If we could assume that $\mathbf{E}'$ represents the applied field $\mathbf{E}$, as in gases at low pressure, we would immediately obtain the static and optical dielectric constants as given in Eqs. 16.11 and 16.12 and thus from Eq. 22.4 the complex permittivity

$$\kappa^* = 1 + \frac{N}{\epsilon_0}\left\{(\alpha_e + \alpha_0) + \frac{\mu^2}{3kT}\frac{1}{1 + j\omega\tau}\right\}. \tag{22.7}$$

Actually, the applied field $\mathbf{E}$ will have to be replaced by some local field $\mathbf{E}'$, for example, the Mosotti field of Eq. 2.9:

$$\mathbf{E}' = \mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0} = \frac{\mathbf{E}}{3}(\kappa^* + 2). \tag{22.8}$$

In this case we obtain for the polarizability per unit volume not the $\kappa^* - 1$ of Eq. 22.7, but the more involved equation

$$\begin{aligned}\frac{N\alpha}{3\epsilon_0} &= \frac{\kappa^* - 1}{\kappa^* + 2}\\ &= \frac{N}{3\epsilon_0}\left\{(\alpha_e + \alpha_a) + \frac{\mu^2}{3kT}\frac{1}{1 + j\omega\tau}\right\}.\end{aligned} \tag{22.9}$$

This modified polarizability has the static and the optical value

$$\begin{aligned}\frac{\kappa_s' - 1}{\kappa_s' + 2} &= \frac{N}{3\epsilon_0}\left\{(\alpha_e + \alpha_a) + \frac{\mu^2}{3kT}\right\},\\ \frac{\kappa_\infty' - 1}{\kappa_\infty' + 2} &= \frac{N}{3\epsilon_0}(\alpha_e + \alpha_a).\end{aligned} \tag{22.10}$$

By introducing the expressions on the left into Eq. 22.9,

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[1] P. Debye, *Polar Molecules*, Chemical Catalog Co., New York, 1929, Chap. V.

we return to the formulation for the complex permittivity given in Eq. 22.4,

$$\kappa^* = \kappa_\infty' + \frac{\kappa_s' - \kappa_\infty'}{1 + j\omega\tau_e}, \tag{22.11}$$

with the new time constant

$$\tau_e = \tau \frac{\kappa_s' + 2}{\kappa_\infty' + 2}. \tag{22.12}$$

Hence, by replacing the applied field **E** with the Mosotti field **E**′ the interpretation but not the shape of the relaxation spectrum has changed. Only the relaxation time has lengthened from τ to τ_e, and the molecular meaning of the static and optical dielectric constants has been altered by the introduction of the denominators $\kappa_s' + 2$ and $\kappa_\infty' + 2$ in Eq. 22.10. Similarly, any other type of local field expression will not change the shape of the absorption spectrum as long as the motion of the dipole molecule is represented by a first-order differential equation.

The remaining problem is the molecular interpretation of the relaxation time τ. According to the assumption of dominating friction, we have to picture the polar molecules as rotating under the torque **T** of the electric field with an angular velocity $\frac{d\theta}{dt}$ proportional to this torque, or

$$\mathbf{T} = \zeta \frac{d\theta}{dt}. \tag{22.13}$$

The friction factor ζ will depend on the shape of the molecule and on the type of interaction it encounters. If one visualizes the molecule as a sphere of the radius a, rotating in a liquid of the viscosity η according to Stokes's law,[2] classical hydrodynamics leads to the value

$$\zeta = 8\pi\eta a^3. \tag{22.14}$$

In a static field, the spherical dipole carriers will have a slight preferential orientation parallel to this field and thus contribute the average moment of Eq. 22.6. A sudden removal of the external field will cause an exponential decay of this ordered state due to the randomizing agitation of the Brownian movement. The relaxation time τ (or τ_e) measures the time required to reduce the order to $1/e$ of its original value. Debye[1] was able to calculate this time statistically by deriving the space orientation under the counteracting influences of the Brownian motion and of a time-dependent electric field and found

$$\tau = \frac{\zeta}{2kT}. \tag{22.15}$$

Combining Eqs. 22.14 and 22.15, Debye obtained for the spherical molecule, if it behaves like a ball rotating in oil, the relaxation time

$$\tau = \frac{4\pi a^3 \eta}{kT} = V\frac{3\eta}{kT}. \tag{22.16}$$

The time constant is proportional to the volume V of the sphere and to the macroscopic viscosity of the solution. Water at room temperature has a viscosity $\eta = 0.01$ poise; with a radius of ca. 2 A for the water molecule, a time constant of $\tau \simeq 0.25 \times 10^{-10}$ sec results.

Figure 22.2 shows that indeed the relaxation time of water is located near the wavelength of 1 cm. The agreement, however, is somewhat marred by the realization that experimentally we have determined $\tau_e \simeq 20\tau$ instead of τ itself. Obviously, neither the sphere model nor the Mosotti field should be taken too seriously; the essence of Debye's approach is to postulate that the orientation of polar molecules in liquids and solids leads spectroscopically to a simple relaxation spectrum.

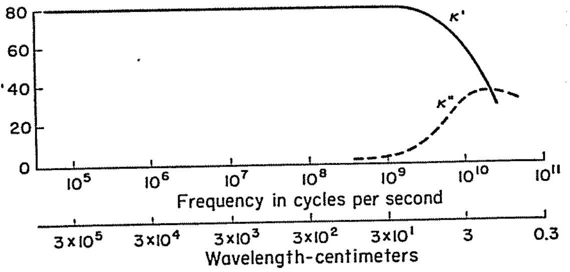

Fig. 22.2. Relaxation spectrum of water at room temperature.

The *Debye equation* (Eq. 22.11) may be written in various forms, which have their special merits for the evaluation of experimental characteristics. Separating it into its real and imaginary parts, we obtain the standard version

$$\begin{aligned} \kappa' - \kappa_\infty' &= \frac{\kappa_s' - \kappa_\infty'}{1 + \omega^2\tau_e^2}, \\ \kappa'' &= \frac{(\kappa_s' - \kappa_\infty')\omega\tau_e}{1 + \omega^2\tau_e^2}, \\ \tan\delta &= \frac{\kappa''}{\kappa'} = \frac{(\kappa_s' - \kappa_\infty')\omega\tau_e}{\kappa_s' + \kappa_\infty'\omega^2\tau_e^2}. \end{aligned} \tag{22.17}$$

If we introduce as a new variable[3]

$$z = \ln \omega\tau_e, \tag{22.18}$$

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[2] G. Stokes, *Trans. Cambridge Phil. Soc. 9*, 8 (1851).

[3] See H. Fröhlich, *Theory of Dielectrics*, Clarendon Press, Oxford, 1949, p. 73.

Eqs. 22.17 may be rewritten in a normalized form

$$\frac{\kappa' - \kappa_\infty'}{\kappa_s' - \kappa_\infty'} = \frac{1}{1 + e^{2z}} = \frac{e^{-z}}{e^z + e^{-z}},$$

$$\frac{\kappa''}{\kappa_s' - \kappa_\infty'} = \frac{1}{e^z + e^{-z}}, \qquad (22.19)$$

$$\frac{\tan \delta}{\kappa_s' - \kappa_\infty'} = \frac{1}{\kappa_\infty' e^z + \kappa_s' e^{-z}}.$$

Figure 22.3 shows this logarithmic plot of the dispersion and absorption characteristic, and, added to them, as a third curve, the relative dielectric conductivity (see I, Eq. 1.16)

$$\sigma = \omega\kappa'' \qquad (22.20)$$

in the normalized form

$$\frac{\sigma\tau_e}{\kappa_s' - \kappa_\infty'} = \frac{e^z}{e^z + e^{-z}}. \qquad (22.21)$$

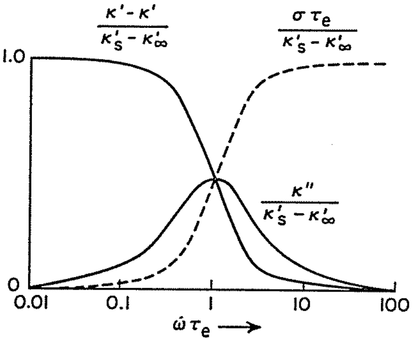

Fig. 22.3. Dielectric constant, loss factor, and conductivity of simple relaxation spectrum in normalized form.

The conductivity curve is the mirror image of the κ' characteristic; that is, the orientation polarization leads to a constant maximum conductivity contribution beyond the range of the dispersion region.

It may seem surprising that, after the polarizing action of the permanent dipoles has disappeared, their existence is still noted with full force as a conduction effect, but the explanation is simple. As the frequencies range so high that the molecules have no time to turn, we do not notice that the two opposite dipole charges are coupled together; their effect on the conduction is therefore the full contribution of two ions of opposite polarity moving in the electric field according to Ohm's law.

Figure 22.3 shows clearly the frequency spread of the dispersion phenomenon. According to the decade scale, it is practically limited to one decade for κ' and to two decades for κ'' above and below the center frequency. One further graphical representation of the Debye equation proves of value in analyzing and extrapolating experimental data. If we plot κ'' against κ' in the complex plane, points obeying the Debye equation fall on a semicircle with its center at $\frac{\kappa_s' + \kappa_\infty'}{2}$ (Fig. 22.4), as Cole and Cole[4] first pointed out. This becomes evident when we rewrite Eq. 22.11 in the form

$$(\kappa^* - \kappa_\infty') + j(\kappa^* - \kappa_\infty')\omega\tau_e = \kappa_s' - \kappa_\infty'. \qquad (22.22)$$

The first member on the left side corresponds to a vector **u**; the second member, as the factor j indicates, adds perpendicular to it and represents a vector **v**; the sum is the diagonal of the circle.

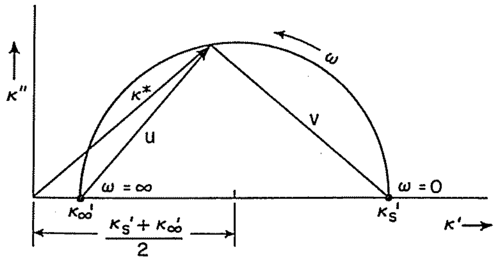

Fig. 22.4. Cole-Cole circle diagram of κ^* in complex plane.

The loss factor κ'' reaches its maximum at the critical frequency

$$\omega_m = 1/\tau_e, \qquad (22.23)$$

that is, at the critical wavelength

$$\lambda_m = 2\pi c\tau_e \qquad (22.24)$$

at which the dipole polarization has fallen to its half value. Furthermore

$$\kappa''_{\max} = \frac{\kappa_s' - \kappa_\infty'}{2} \equiv \frac{S}{2}. \qquad (22.25)$$

The relaxation time and the contribution S of the orientation polarization to the permittivity can be determined by these relations from the absorption characteristic of a dielectric as long as the Debye equation is valid.

Finally, from Eq. 22.17 we obtain the linear equation in κ' versus $\omega\kappa''$, and κ' versus κ''/ω:

$$\kappa' = \kappa_s' - \omega\tau_e\kappa'',$$
$$= \kappa_\infty' + \frac{\kappa''}{\omega\tau_e}, \qquad (22.26)$$

the first of which may be rewritten

$$\epsilon' = \epsilon_s' - \sigma\tau_e. \qquad (22.27)$$

Thus the static and optical dielectric constants are given by the intersection, and τ_e by the slope of a

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[4] K. S. Cole and R. H. Cole, *J. Chem. Phys. 9*, 341 (1941).

straight line, as long as the simple relaxation equation applies.

The theory has confronted us with two extreme cases: the classical resonance absorption[5] in a quantum-mechanical reinterpretation and the Debye relaxation absorption. It is tempting to link the two cases graphically by postulating that pressure broadening gradually converts a resonance into a relaxation spectrum (Fig. 22.5). Also mathematically the semblance of a unified theory can be achieved, as the interesting attempt of Van Vleck and Weisskopf[6] shows (extended by Van Vleck and Margenau[7]). However, it seems questionable how far it makes physical sense to force a marriage between two concepts based on entirely different assumptions. The original resonance picture deals with oscillators that are effectively uncoupled and suffer only now and then disturbing impacts. The force of the applied field induces moments, and the frequency of the field changes these moments in amplitude and phase. The relaxation picture deals with rotators in a state of perpetual impact. The field produces a torque on permanent moments, and the orientation of these moments begins to lag as the frequency increases. There is no classical resonance absorption for the rotator, and the replacing of induced moments by permanent moments in the resonance equation does not change the original meaning of the frequency dependence, which is not compatible with that of the relaxation equation. We should expect that the pressure broadening of rotation spectra does not lead to a unique result as Fig. 22.5 implies, but to a diversity of situations in keeping with the great variety of surroundings which the solid and liquid state can offer. The Debye case is one simple prototype of the behavior of polar molecules in condensed phases; we shall encounter others in the subsequent sections.

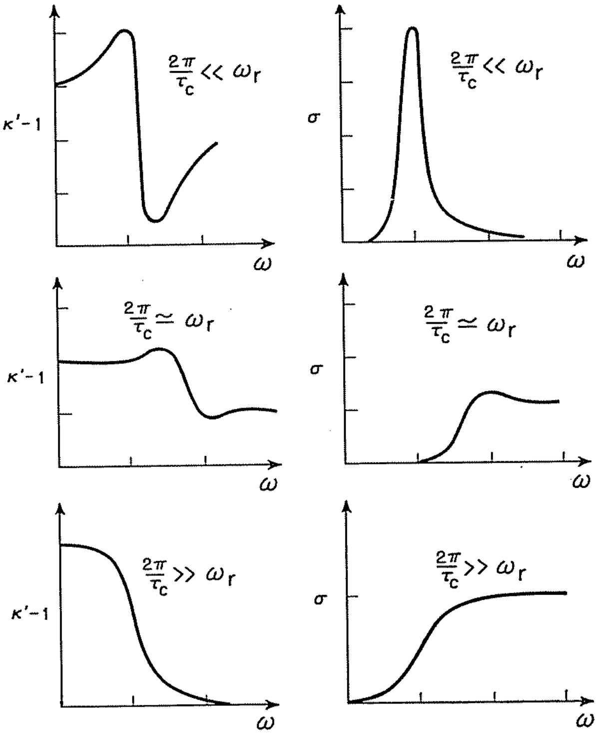

Fig. 22.5. Assumed pressure broadening of resonance into relaxation spectrum (collision frequency very much smaller, equal, or much larger than the rotation frequency).

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[5] The classical dispersion equations were first derived by Ketteler and Helmholz [see E. Ketteler, *Wied. Ann. 49,* 382 (1893)] and developed into an electron theory of dispersion by Lorentz (see H. A. Lorentz, *Proceedings Amsterdam Academy,* 1897–1898).

[6] J. H. Van Vleck and V. F. Weisskopf, *Revs. Mod. Phys. 17,* 227 (1945).

[7] J. H. Van Vleck and H. Margenau, *Phys. Rev. 76,* 1211 (1949).

23 · The Mosotti Catastrophe and the Local Field

The assumption of a simple relaxation spectrum fits satisfactorily the frequency response of a number of dielectrics, especially of dilute solutions of polar materials in nonpolar solvents, when the shape of the dipole molecules is approximately spherical. This fact, however, should not be construed as a confirmation of the special Debye equation (Eq. 22.11), which is based on the Mosotti field (Eq. 2.9). By specifying this type of local field we have implicitly resigned ourselves to catastrophic consequences.

This becomes apparent when we return to the defining equation for the polarization (Eq. 1.5)

$$\mathbf{P} = (\kappa' - 1)\epsilon_0\mathbf{E} = N\alpha\mathbf{E}'. \tag{23.1}$$

By introducing for the local field $\mathbf{E}'$ the Mosotti field

$$\mathbf{E}' = \mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0}, \tag{23.2}$$

we obtain for the polarization and the electric suscep-