

POLARIZATION ELLIPTICITY OF LIGHT REFLECTED FROM A LIQUID SURFACE

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If a beam of plane-polarized light is incident on a liquid surface, the reflected beam displays a slight polarization ellipticity, while Fresnel theory predicts that the plane polarization will be preserved. There have been several theoretical and experimental studies of this topic [1-8], and the general consensus is that the polarization ellipticity results from the existence of a surface layer having a structure different from that of a homogeneous liquid.

In the case in which the light in the incident beam is polarized in a plane making an angle of 45° with the incidence plane, the ellipticity ρ is

$$\rho = \frac{\pi}{\lambda} \sqrt{n^2 + 1} (\gamma_x - \gamma_z), \quad (1)$$

where λ is the wavelength of the light; n is the refractive index of the homogeneous liquid for the given wavelength; γ_x and γ_z are theoretical parameters which depend on neither the wavelength nor the light intensity,

$$\gamma_i = \frac{\tau_i}{\mathcal{P}_i}, \quad (2)$$

τ_i are the components of the induced dipole moment per unit area of the surface layer; \mathcal{P}_i are the components of the polarization of the homogeneous liquid.

The vector $\vec{\mathcal{P}}$ can be found from the macroscopic equations for the electric field in a homogeneous dielectric. In determining the dipole moment of the surface layer we must take into account the layer structure and thus employ a specific model for the liquid structure. For this purpose we will use the method of molecular distribution functions.

Far from the critical point, where we can neglect the interaction between the molecules of the vapor and those of the liquid, we can get satisfactory results by using the model of a liquid bounded by an ideal impenetrable wall. For this model approximate solutions are available with which we can find the single-component distribution function $F_1(\mathbf{q})$ and the binary distribution $F_2(\mathbf{q}', \mathbf{q})$ in the surface layer if we know the binary molecular interaction potential and the radial distribution function for the homogeneous liquid, $g(|\mathbf{q}' - \mathbf{q}|, \cdot)$. We place the origin of coordinates at a point such that the XOY plane coincides with the wall and the z axis is directed from the vapor into the liquid.

The dipole moment of the surface layer consists of the dipole moments $\mathbf{P}_0(z)$ of the molecules in the layer; we can therefore write the components of the vector τ as

$$\tau_i = \frac{l}{v} \int_0^l P_{0i}(z) F_1(z) dz, \quad (3)$$

where v is the average volume per molecule in the homogeneous liquid; l is the thickness of the surface layer.

For nonpolar liquids the molecular dipole moment $\mathbf{P}_0(z)$ arises as a result of the electric field $\mathbf{E}(z)$ which consists of the field \mathbf{E}_0 of the light wave and that $\mathbf{E}_1(z)$ of the surrounding dipoles. In the visible part

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of the spectrum the wavelength is much higher than the linear dimension a of the molecules (by two or three orders of magnitude), so we can assume that the field intensity is the same at a given instant at all points in the surface layer, which is no more than a few molecular diameters thick. The instantaneous values of the molecular dipole moment and the field acting in this case are related by the usual relation

$$P_0(z) = \beta E(z), \quad (3')$$

where β is the average polarizability of the liquid molecules.

The field $E_1(z)$ can be expressed in terms of the conditional distribution function $F_1(q'/q)$, which gives the probability for finding a molecule at point q' if there is a molecule at point q . We denote the difference between q' and q as r ; then we have

$$E_1(z) = \frac{1}{v} \int \left[\frac{3(P_0(z), r) r}{r^5} - \frac{P_0(z)}{r^3} \right] F_1(q'/q) dq'. \quad (4)$$

The conditional distribution function $F_1(q'/q)$ is related to the single-component function $F_1(q)$ and the binary function $F_2(q', q)$ by

$$F_1(q'/q) = F_2(q', q)/F_1(q).$$

In the superposition approximation, we can express the binary distribution function in the surface layer in terms of the single-component functions at points q and q' and the radial distribution function of a homogeneous liquid:

$$F_2(q', q) = F_1(q') F_1(q) g(r).$$

Then we have

$$E_1(z) = \frac{1}{v} \int_{z' > 0} \left[\frac{3(P_0(z), r) r}{r^5} - \frac{P_0(z)}{r^3} \right] g(r) F_1(z') dq', \quad (5)$$

where the integration is carried out over the entire $z' > 0$ half-space, since a dipole at $z' = z$ is automatically included (since we have $g(r < a) \equiv 0$).

After lengthy calculations, we find integral equations for the components of the dipole moment of a molecule in the surface layer at a distance z from the wall:

$$P_{0i}(z) = \beta E_{0i} + C_i \int_0^\infty P_{0i}(z') F_1(z') Q(|z - z'|) dz'. \quad (6)$$

In Eq. (6), we have

$$C_x = \frac{\pi\beta}{v}; \quad C_z = -\frac{2\pi\beta}{v}; \quad Q(|z - z'|) = \int_{|z-z'|}^\infty \frac{g(r) [r^2 - 3(z - z')^2]}{r^4} dr.$$

In the interior of the liquid, as $z \rightarrow \infty$, the dipole moment components take on the constant values $P_{0i\infty}$, and the integral $\int_0^\infty dz' Q(|z - z'|)$ becomes equal to $4/3$. For $P_{0i\infty}$ we thus find the standard expression, found by Lorentz for isotropic media. We can therefore transform from E_{0i} to $P_{0i\infty}$:

$$P_{0i}(z) = \left(1 - \frac{4}{3} C_i\right) P_{0i\infty} + C_i \int_0^\infty P_{0i}(z') F_1(z') Q(|z - z'|) dz'.$$

For many nonpolar liquids we have $C_i < 1$. We expand $P_{0i}(z)$ in a series in terms of C_i :

$$P_{0i}(z) = P_{0i}^{(0)}(z) + C_i P_{0i}^{(1)}(z) + C_i^2 P_{0i}^{(2)}(z) + \dots + C_i^k P_{0i}^{(k)}(z) + \dots$$

We substitute this expansion into (7) and equate the coefficients of identical powers of C_i^k on the two sides of the resulting equation. In this manner we find the $P_{0i}^{(k)}(z)$:

$$P_{0i}^{(0)}(z) = P_{0i\infty},$$

TABLE 1. $t = 20^\circ\text{C}$, $\lambda = 5460 \text{ \AA}$

Substance	$\rho \cdot 10^5$ theo	$\rho \cdot 10^5$ exp	Substance	$\rho \cdot 10^5$ theo	$\rho \cdot 10^5$ exp
Benzene	122	107–136	n-Pentane	92	70
Toluene	130	114	n-Octane	122	92
Carbon tetra- chloride	114	84–126	Cyclopentane	104	121
p-Xylene	133	129	Chlorobenzene	135	138
n-Hexane	105	65	Water	57	40–75

$$P_{0i}^{(1)}(z) = -\frac{4}{3}P_{0i\infty} + P_{0i\infty} \int_0^\infty F_1(z') Q(|z-z'|) dz',$$

$$P_{0i}^{(\kappa)}(z) = \int_0^\infty F_1(z') Q(|z-z'|) P_{0i}^{(\kappa-1)}(z) dz'. \quad (7)$$

Accordingly, the dipole moment of a molecule in the surface layer can be expressed in terms of its value in a homogeneous liquid:

$$P_{0i}(z) = P_{0i\infty} \left\{ \left(1 - \frac{4}{3} C_i \right) + C_i \int_0^\infty F_1(z') Q(|z-z'|) dz' + C_i^2 \int_0^\infty F_1(z') Q(|z-z'|) dz' \left[-\frac{4}{3} + \int_0^\infty F_1(t) Q(|t-z|) dt \right] + \dots \right\}. \quad (8)$$

The components of the vector \mathbf{P} can be written as

$$P_i = \frac{1}{v} P_{0i\infty} F_{1(\infty)}.$$

Since the integrals associated with the high powers of C_1^κ fall off rapidly with increasing κ , we can restrict Eq. (7) to the first approximation, i.e., take into account only the first two terms. Substituting into (2) the components $P_{0x}(z)$ and $P_{0z}(z)$, we find

$$\gamma_x - \gamma_z = (C_z - C_x) \int_0^t F_1(z) \left[-\frac{4}{3} + \int_0^\infty F_1(z') Q(|z-z'|) dz' \right] dz. \quad (9)$$

Substituting (9) into (1), we find the final expression for the ellipticity ρ :

$$\rho = \frac{4\pi^2\beta}{\lambda} \sqrt{n^2+1} \int_0^\infty F_1(z) dz \left[1 - \frac{3}{4} \int_0^\infty F_1(z') Q(|z-z'|) dz' \right]. \quad (10)$$

We used Eq. (10) to calculate ρ for several liquids*; the results are shown in Table 1. Also shown in this table are experimental data from [3-5]. Since there is a large scatter in the experimental values obtained for ρ for certain liquids by various investigators, we show the corresponding ranges.

Comparison shows that the values of ρ calculated from Eq. (10) agree quite satisfactorily with experimental values not only for the nonpolar liquids, but also for liquids whose molecules have a rigid dipole moment, i.e., water, chlorobenzene, etc. We can explain this result by assuming that the oscillation period of the electric field of the light wave is much lower, by about two orders of magnitude, than the

* The radial distribution function was taken from [10], and the single-component distribution function was calculated from the approximate equation given in [11]:

$$F_1(z) = 1 - \frac{2\pi}{v} \int_z^\infty dt \int_{|t|}^\infty [g(t) - 1] r dr.$$

orientational-relaxation time of many polar molecules. Because of this circumstance, the electronic polarizability of the molecules plays the main role in producing the induced dipole moment and the polarization ellipticity of the reflected light.

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