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OPTICAL PROPERTIES OF LIQUIDS UNDER PRESSURE (*)

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Résumé. — Les très récentes mesures de Vedam et Limsuwan (1975, 1977) sur l'index de réfraction de l'eau, du tétrachlorure de carbone, de l'n-hexane et de l'n-pentane à hautes pressions sont étudiées au moyen d'une nouvelle théorie qui donne la dépendance de la polarisabilité moléculaire en fonction de l'état thermodynamique du liquide. Parmi toutes les formules rencontrées dans la littérature auxquelles la théorie est appliquée, celle déduite par l'auteur (1976) se démontre la plus apte à expliquer les données expérimentales.

Abstract. — The recent data of Vedam and Limsuwan (1975, 1977) on the refractive indices of water, carbon tetrachloride, n-hexane and n-pentane under pressure are discussed in the light of a new model giving the dependence of the molecular polarizability on the thermodynamical state of the liquid. Among all the equations currently met in the literature to which the model is applied, the formula previously deduced by the author (1976) is shown to provide the best explanation of the experimental data.

1. **Introduction.** — In recent years, by the use of a high pressure interferometer, Vedam and Limsuwan (V. L.) have brought a remarkable contribution to the knowledge of the optical properties of dielectric liquids under pressure. As a preliminary result in this field, they gave first the pressure dependence of the refractive index of water and carbon tetrachloride [1] and, more recently, of n-pentane and n-hexane [2]. It is the purpose of this paper to discuss their data in terms of the current theories of the refractive index : these will be applied to a new model giving the dependence of the molecular polarizability on the thermodynamical state of the liquid. In such a way it will be possible to give a satisfactory microscopic interpretation of the optical behaviour of liquids under pressure without resorting to the empirical relation between refractive index and Lagrangian strain, as suggested by the authors cited in reference [1].

2. Survey of the principal theories of refractive index.

— Since in the range of optical frequencies the permanent dipoles associated with the molecules of the liquid cannot follow the oscillations of the applied field, the response of the system to such a field is not affected by the presence of the permanent dipoles :

the system behaves like a non-polar liquid, composed of polarizable particles (with polarizability α) without an intrinsic dipole moment. As a consequence, the theory of the refractive index for any liquid becomes formally the theory for the dielectric constant of a non-polar liquid (with $\epsilon = n^2$). For this reason, the formulae existing in the literature can be classified in terms of four types, namely :

— The Lorentz-Lorenz formula (an extension to the optical case of the Clausius-Mossotti equation)

$$\frac{n^2 - 1}{n^2 + 2} = Z \quad (1)$$

where

$$Z = \frac{4}{3} \pi \bar{n}^0 \alpha \quad (2)$$

\bar{n}^0 being the average number of molecules per unit volume.

— The Onsager-Böttcher equation (Ref. [3], p. 59), that will be written in the unusual form

$$\frac{9 n^2}{(n^2 - 1)(2 n^2 + 1)} + \frac{2(n^2 - 1)}{(2 n^2 + 1) \eta} = \frac{1}{Z} \quad (3)$$

in terms of the packing fraction

$$\eta = \frac{\pi}{6} \bar{n}^0 \sigma^3 \quad (4)$$

where σ is the diameter of the spherical molecule.

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— The Fuller Brown equation (Ref. [3], p. 74) we should have

$$\frac{n^2 + 2}{n^2 - 1} = \frac{1}{Z} + \left(\frac{15}{16} - \frac{1}{4\eta} \right) Z \quad (5)$$

derived from the rigorous statistical theory of a dielectric non-polar fluid, after introducing the two main approximations : a) the three-molecule distribution function is expressed in terms of pair distribution functions through the Kirkwood superposition approximation $g_{123} = g_{12} g_{23} g_{31}$, b) the pair distribution function is oversimplified by the use of a step function, so that $g(r) = 0$ for $r \leq \sigma$, $g(r) = 1$ for $r > \sigma$.

— The formula deduced by the author [4] in the frame of a general theory of dielectric liquids [4-8], by a truncated Fourier expansion of the dipole-dipole interaction :

$$n^2 - 1 = 3Z \frac{1 + Z[3 + F(Z)]}{(1 + 3Z)(1 - \gamma Z) + \gamma Z F(Z)} \quad (6)$$

where

$$\gamma = (1 - \bar{n}^0 \chi k_B T)^{-1}, \quad (7)$$

$$F(Z) = 1 + 0.1756 \frac{3Z}{1 + 3Z}$$

χ being the isothermal compressibility of the liquid.

It should be noted that while eqs. (2), (3) and (5) are in principle applicable to the gaseous, liquid and solid states of matter, eq. (6) was specifically derived for the liquid state.

The Onsager-Böttcher and the Fuller Brown equations have been generally used to study the dielectric constant of non-polar fluids, although their application to refractive indices is not new (Ref. [3], p. 118). In principle, they are less reliable than eqs. (1) and (6), as the presence of the packing fraction η introduces an adjustable parameter, whose exact definition remains an open question. In most applications of eqs. (3) and (5) to dielectric constants, σ is determined by applying least squares analysis to high pressure data (see Böttcher [9] and Fuller Brown, Ref. [3], p. 61) : however, a similar procedure is obviously inadequate to *predict* the dielectric behaviour (and therefore the optical behaviour) under pressure. The reliability of such equations is therefore strictly related to the possibility of assigning a definite value to the packing fraction of the liquid, in a way independent of the observed pressure dependence of n , which must be explained by the equations themselves.

The problem does not seem to exist for eq. (5), that was deduced under a well defined assumption concerning the pair distribution function $g(r)$. Since $g(r)$ must satisfy the Ornstein-Zernike fluctuation theorem [10]

$$4\pi\bar{n}^0 \int_0^\infty [g(r) - 1] r^2 dr = \bar{n}^0 \chi k_B T - 1 \quad (8)$$

$$\frac{-4\pi}{3} \bar{n}^0 \sigma^3 = \bar{n}^0 \chi k_B T - 1$$

or also, from eqs. (4) and (7)

$$\eta = \frac{1}{8\gamma}. \quad (9)$$

However, γ is always very close to unity, so that eq. (9) predicts for the packing fraction a value which is essentially independent of the liquid under study, and also of its thermodynamical state. This is clearly an unacceptable result, particularly as the value $\frac{1}{8} = 0.125$ is very far from the range $0.3 \div 0.5$, which is expected to be typical of the liquid state. The inconsistency of the value given by eq. (9) is confirmed by the inadequacy of eqs. (5)-(9) to explain the observed optical behaviour of liquids (see section 4). Consequently, to rescue eq. (5), η must be treated as a model parameter to be taken from some other source : however in this case eq. (8) is no longer satisfied. These criticisms do not apply to eqs. (1) and (6), where the parameter η is not involved : this is especially true for eq. (6), which was derived through a procedure fully consistent with the Ornstein-Zernike theorem.

As for the Onsager-Böttcher equation, it avoids the introduction of a pair correlation function, because the molecule of diameter σ is embedded in the dielectric continuum. Eq. (5) is therefore always independent of eq. (8), but the problem of an exact definition of σ , and therefore of η , particularly for molecules with non-spherical shape such as those involved in organic liquids, still remains unsolved. For these reasons the theoretical interpretation of the refractive index data under pressure should be confined to a discussion based on the two competing formulae (1) and (6). Nevertheless, in order to include eqs. (3) and (5) also in our analysis, we will adopt for η the expression given by the Percus-Yevick (P. Y.) theory of liquids [11-14]

$$\bar{n}^0 \chi k_B T = \frac{(1 - \eta)^4}{(1 + 2\eta)^2}; \quad (10)$$

though of course not fully consistent with the assumptions lying at the basis of Fuller Brown equation, the value $\eta_{P.Y.}$ given by eq. (10) is the best estimate at our disposal for the packing fraction of a liquid.

3. Pressure and temperature dependence of the polarizability. — If we confine ourselves to the Yvon-Kirkwood model of a dielectric liquid, where the polarizability α is assumed to be independent of the thermodynamical state of the liquid, then $Z = Z_0 \rho / \rho_0$, where Z_0 must be determined by inserting into the formula under study the experimental refractive index n_0 corresponding to the thermodynamical state at atmospheric pressure with density ρ_0 . When Z_0

is known, the same formula predicts the refractive index for any other thermodynamical state with density ρ . Such a procedure was successfully used in references [4, 7 and 8] : but is α really a molecular constant ? For moderately low pressures (< 1 kbar), this assumption is supported by its capability of explaining through eq. (6) the temperature and pressure dependence of the refractive indices and dielectric constants for a wide class of liquids. However, as we reach pressures of the order of 10 kbar, it is reasonable to ask how far the above approximation can be justified.

On physical grounds, the departure of α from its value α_0 in vacuo (deducible through refractive index measurements on rarefied gases) is due to the perturbation introduced on the electron cloud of the molecule by its interaction with the other molecules of the liquid. Such an interaction can be simply described from a classical point of view in terms of pressure forces applied by the environment to the molecular surface. In other words, only the external layer of the molecule is assumed to take part in the direct interaction with the other molecules. Under these circumstances it is useful to introduce (for spherical molecules) a scalar parameter p , giving the force per unit area by which the molecular surface interacts with the rest of the liquid. p can be positive (for the case of inward radial forces, tending to reduce the molecular volume), or negative (for the case of outward forces, tending to increase the molecular volume). In this picture the electronic polarizability is regarded as a function of p and expanded to first order in p , namely $\alpha = \alpha_0 + (\mathrm{d}\alpha/\mathrm{d}p)_0 p$. Dividing by α_0 one gets

$$\frac{\alpha - \alpha_0}{\alpha_0} = \left(\frac{1}{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{d}p} \right)_0 p = \left(\frac{1}{V} \frac{\mathrm{d}V}{\mathrm{d}p} \right)_0 \times \left(\frac{V}{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{d}V} \right)_0 p = -K \left(\frac{\mathrm{d} \ln \alpha}{\mathrm{d} \ln V} \right)_0 p \quad (11)$$

where $V = \pi\sigma^3/6$ is the volume of the molecule, and $K = -(V^{-1} \mathrm{d}V/\mathrm{d}p)_0$ is its compressibility modulus. The coefficient $(\mathrm{d} \ln \alpha / \mathrm{d} \ln V)_0$ is unity when the electronic cloud is assumed to be uniformly distributed through the molecular volume (Mossotti and Thomson models, for which $\alpha = (\sigma/2)^3$, see [3], p. 9). In the general case, its modulus is expected to be of the order of unity (section 5.2).

We can try to evaluate p explicitly using the model developed by Longuet-Higgins and Widom (L.-H. W.). The fundamental concept of their theory is that the structure of a liquid is determined primarily by the repulsive forces between molecules, and that the main effect of the attractive forces between molecules is to provide a uniform background potential in which the molecules move. Such a potential does not contribute to the pair correlation function $g(r)$ (and consequently to any bulk property depending on $g(r)$, such as the structure factor of the liquid). $g(r)$ can therefore be taken from the P. Y. theory [14], or from the scaled

particle theory [16], that simply treats the liquid as a system of hard spheres. The only effect of the background potential, generally written as $-2a\tilde{n}^0$, is shown to be a pressure term of the van der Waals type $+a(\tilde{n}^0)^2$, which must be added to the applied pressure in the equation of state (see below).

In the framework of the above model, the pressure p acting on the surface of a bulk molecule is clearly made of two terms : 1) a negative term due to the attractive forces exerted by the uniform distribution of matter with molecular number density \tilde{n}^0 ; and 2) a positive term, describing the effect of the molecules colliding with the reference molecule in unit time. The first term is of the type $-A\tilde{n}^0$, where

$$A = \pi \int_0^\infty f(r) r^2 \mathrm{d}r \quad (12)$$

$f(r)$ being the modulus of the attractive force exerted on the unit area of the molecular surface by a molecule at a distance r from it. The second term is simply obtained by noting that, for symmetry reasons, the total average force imparted by the environment to the reference molecule is zero, so that on the average this can be assumed to be fixed at the origin. Under these circumstances the scattering of the surrounding molecules is completely elastic, and the average momentum transferred to the unit area of the molecular surface per unit time (i.e. the pressure) is $m \langle v_n^2 \rangle \tilde{n}(\sigma)$, where v_n is the velocity component along a direction normal to the selected unit area, m is the mass of the molecules, and $\tilde{n}(\sigma) = \tilde{n}^0 g(\sigma)$ is the contact number density. Now since

$$m \langle v_n^2 \rangle = k_B T,$$

we obtain from (11) :

$$\frac{\alpha - \alpha_0}{\alpha_0} = K \left(\frac{\mathrm{d} \ln \alpha}{\mathrm{d} \ln V} \right)_0 [A\tilde{n}^0 - k_B T\tilde{n}(\sigma)]. \quad (13)$$

To link A with the parameter a appearing in the van der Waals pressure term, we point out that the net force acting on a molecule at the surface of the liquid, as a result of the attractive pressure forces, is $\pi(\sigma/2)^2 A\tilde{n}^0$. This is an inward force, which on the average is applied to all the molecules contained in a surface layer with thickness l of the order of the intermolecular distance : for symmetry reasons, as we enter the bulk of the liquid, the resultant of the attractive pressure forces on a molecule becomes zero. Therefore, the net force associated with the unit area of the liquid surface is $Al\pi(\sigma\tilde{n}^0/2)^2$, which is exactly of the van der Waals type and we have

$$a = Al\pi \left(\frac{\sigma}{2} \right)^2. \quad (14)$$

This equation will be used in section 5.

We now recall the thermal equation of state for hard spheres, as derived from a straightforward

application of the virial theorem to a fluid of particles interacting *via* the potential $U(r) = +\infty$ ($r \leq \sigma$), $U(r) = 0$ ($r > \sigma$), and subjected to an external pressure \tilde{P} on the surface [17, 18] :

$$\frac{\tilde{P}}{\tilde{n}^0 k_B T} = 1 + \frac{2\pi}{3} \tilde{n}^0 \sigma^3 g(\sigma). \quad (14')$$

Clearly, the effect of the background attractive potential must be included in \tilde{P} , which turns out in this way to be the sum of the applied pressure P and of the van der Waals term $a(\tilde{n}^0)^2$. If we use for $g(\sigma)$ the result of the P. Y. theory or of the scaled particle theory [14] (which gives answers consistent with the P. Y. theory), namely

$$g(\sigma) = \frac{3}{2\pi\sigma^3 \tilde{n}^0} \left[\frac{1 + \eta + \eta^2}{(1 - \eta)^3} - 1 \right] = \frac{1}{4\eta} \left[\frac{1 + \eta + \eta^2}{(1 - \eta)^3} - 1 \right] \quad (15)$$

we get

$$[P + a(\tilde{n}^0)^2]/(\tilde{n}^0 k_B T) = (1 + \eta + \eta^2)/(1 - \eta)^3 \quad (16)$$

which is the Longuet-Higgins and Widom's equation. Therefore, in the framework of the theory developed by these authors, eq. (15) can be consistently introduced into (13). In order to derive η , it is necessary to recall the Ornstein-Zernike theorem (8), for which the isothermal compressibility is entirely determined by the knowledge of $g(r)$. Since the L.-H. W. model uses the P. Y. pair correlation function, the formal expression for χ for this model must be the same as for the simple P. Y. hard sphere liquid, namely eq. (10). Consequently, *the parameter η appearing in eq. (15) must be deduced from eq. (10)*, by the use of the experimental values of χ . The corresponding values of σ obtainable from eqs. (4)-(10) will be denoted by σ^* .

Eq. (10) does not contradict eq. (16) : if one uses (16) to calculate $\chi = (\tilde{n}^0)^{-1} (\partial \tilde{n}^0 / \partial P)_T$ one finds exactly eq. (10) provided that

$$\left(\frac{\partial a}{\partial \tilde{n}^0} \right)_T = -\frac{2a}{\tilde{n}^0} + \frac{\pi}{2} k_B T (\sigma^*)^2 \left(\frac{\partial \sigma^*}{\partial \tilde{n}^0} \right)_T \frac{4(1 + \eta) + \eta^2}{(1 - \eta)^4}. \quad (17)$$

This relation gives the density dependence of a , when the density dependence of σ^* has been determined through eq. (10). All the quantities appearing on the right hand side are available from sections 4 and 5 of this paper for water, n-hexane, n-pentane and carbon tetrachloride. Direct substitution of their numerical values into eq. (17) shows that for all the liquids $(\partial a / \partial \tilde{n}^0)_T$ is negative : this result is in agreement with the interpretation of a given by eq. (14), because both l and σ are expected to decrease when the density

risks ⁽¹⁾. On the contrary $(\partial \sigma^* / \partial \tilde{n}^0)_T$ is always found to be positive : consequently, the quantity

$$[\partial a / \partial \tilde{n}^0 + 2a / \tilde{n}^0]_T (\tilde{n}^0)^2 = \{ \partial [a(\tilde{n}^0)^2] / \partial \tilde{n}^0 \}_T$$

which according to eq. (17) has the same sign as $(\partial \sigma^* / \partial \tilde{n}^0)_T$, is positive. We conclude that for all the liquids treated in section 4 the pressure term $a(\tilde{n}^0)^2$ increases with density, but more slowly than one could argue from the simple van der Waals quadratic law.

The use of eq. (10) for the determination of η (or σ) goes back to Ashcroft and Lekner (A. L.) [13], who explained the electrical resistivities of liquids metals by treating the metal ions as hard spheres. Using a procedure quite analogous to that followed here, Ashcroft and Lekner employed the values of σ resulting from (10) to calculate $g(r)$ (or more precisely, the structure factor $a(k)$ of the liquid, which involves the Fourier transform of $g(r)$). Actually, the values we have denoted by σ^* are always found to be in reasonable agreement with independent estimates of the molecular diameters based on X-ray scattering data. Their slight change with density (see section 4) is due to the fact that σ^* plays the role of an effective diameter, owing to the presence in real liquids of the attractive intermolecular forces, which have not been explicitly included into the P. Y. pair correlation. This is clearly shown by eq. (17), where the density dependence of σ^* is intrinsically related to the density dependence of the pressure term $a(\tilde{n}^0)^2$ due to attractive forces. In liquids, the effect of these forces is enhanced at moderately low densities, where they become comparable in magnitude with the repulsive part of the interaction : on the contrary, the latter is expected to dominate as we reach the high density region. In a model where the whole interaction is described in terms of one parameter (σ^*), measuring the spatial extension of the repulsive part, this amounts to saying that σ^* must decrease when the density is reduced, i.e. $(\partial \sigma^* / \partial \tilde{n}^0)_T > 0$. As pointed out previously, such a behaviour of σ^* is actually observed for all the liquids.

From the above discussion it is clear that the pressure dependence of the effective diameter σ^* must not be confused with that of the real diameter of the molecule, varying according to the law $\delta\sigma/\sigma = -\frac{1}{3} Kp$: the model parameter σ^* obtained from (10) has merely to be considered as a useful tool to calculate $g(\sigma)$, which is the quantity of physical interest required by the theory (Eq. 13). By identifying $g(\sigma)$ with $g(\sigma^*)$ any inconsistency deriving from the unphysical rise of σ^* with pressure disappears because the resulting function $g(\sigma^*)$ (i.e. function (15) with η given by (10)) shows a qualitatively correct density dependence,

⁽¹⁾ The parameter σ appearing in eq. (14) is obviously the real diameter of the molecule, which must be reduced by an increase in the density (compression). For the reasons outlined below, it is in principle slightly different from σ^* , which plays the role of an effective diameter, useful only for the calculation of $g(\sigma)$.

consisting of a marked rise with \tilde{n}^0 . The identification of σ with σ^* is allowed if σ enters the theory only through $g(\sigma)$: this is the case of Lorentz-Lorenz equation (1) and of author's equation (6), which do not explicitly contain σ . Things go differently for eqs. (3) and (5), where σ is directly called into play as the real diameter of the molecule: in this case the approximation $\sigma = \sigma^*$, implied by the adoption of eq. (10) for η , appears less reasonable.

Putting

$$A^* = \frac{K\alpha_0 AN}{M} \left(\frac{d \ln \alpha}{d \ln V} \right)_0 \quad (18)$$

$$C^* = \frac{K\alpha_0 k_B N}{M} \left(\frac{d \ln \alpha}{d \ln V} \right)_0 \quad (19)$$

where N is Avogadro's number, and M the molecular weight, we can rewrite eq. (13) in the final form

$$\alpha = \alpha_0 + A^* \rho - C^* \rho T g(\sigma). \quad (20)$$

It is reasonable to characterize the normal behaviour of a molecule by $(d \ln \alpha / d \ln V)_0 > 0$: this condition is in agreement with the classical Mossotti and Thomson models, leading to the simple formula $\alpha = (\sigma/2)^3$. Under these circumstances, both the constants A^* and C^* are positive, and since in the liquid phase the repulsive term $-C^* \rho T g(\sigma)$ is expected to dominate, α must be a decreasing function of the applied pressure. This is actually the case for water, n-hexane and n-pentane (see next section): on the contrary, we will reach the exactly opposite conclusion (α rising with pressure, and $(d \ln \alpha / d \ln V)_0 < 0$) for carbon tetrachloride. The anomalous behaviour of this liquid, which certainly cannot be explained in terms of the simple Mossotti and Thomson models, will be briefly discussed in section 5.7.

Finally, we point out that the free-molecule-polarizability α_0 is simply related to the refractive index n_g of the substance in its gaseous or vapour state by the equation

$$n_g^2 - 1 = 2 \pi N \alpha_0 / V_M \quad (21)$$

where V_M is the molar volume. Eq. (21) implies the identity of the local field with the macroscopic electric field, a condition which is certainly verified in the low density limit: under these circumstances the right

hand side of eq. (21) is so small that the approximation $n_g^2 - 1 \simeq 2(n_g - 1)$ used to deduce eq. (21) is widely satisfied. In the literature, the experimental refractive index is often referred to an ideal gas at 0 °C, 760 mmHg, made of molecules with polarizability deduced from (21): in other words

$$n^* - 1 = 1.688 \, 43 \times 10^{20} \alpha_0 \quad (\alpha_0 \text{ in cm}^3). \quad (22)$$

The parameter n^* will be extensively used in the next section.

4. Application of the theory to real liquids. — The theory developed in section 3 is now applied to the four liquids investigated by V. L. The three constants α_0 , A^* and C^* appearing in eq. (20) can be determined for each liquid by fitting the particular formula under study (Eqs. (1) to (6)) so as to reproduce the absolute values of n corresponding to three representative states of the liquid: two of these are chosen at atmospheric pressure (and different temperatures), the third at a pressure slightly higher (i.e. the minimum pressure above 1 atm. for which refractive index data are available). At this point, eq. (20) itself is able to provide the value of the polarizability at any desired pressure and temperature, and consequently eqs. (1)-(6) can be used to predict the high pressure behaviour of the refractive index of liquids. In the meantime, the knowledge of α_0 allows one to predict, through eq. (22), the ideal gas refractive index n^* .

4.1 WATER. — The three density values referring to 25 °C, as listed in table I, are consistent with the particular form of Tait's equation

$$\frac{\rho_0}{\rho} - 1 = -C \log_{10} \frac{B + P}{B + P_0} \quad (23)$$

with $C = 0.315 \, 0$, $B = 2.996$ kbar, given by Gibson and Loeffler (G. L.) [19]. In eq. (23) ρ_0 is the density at atmospheric pressure (P_0). We take ρ_0 at 25 °C from Ref. [20], F-5, which provides the temperature dependence of ρ and χ at 0.001 kbar according to the recent measurements of Kell [21]. From the same source we deduce the density at 71 °C. The reason of the choice of this particular temperature is the following. There is a very slight discrepancy between the compressibility values at 0.001 kbar, 25 °C, as given by G. L.

TABLE I

Density and compressibility data for water

P (kbar)	t (°C)	ρ (g.cm ⁻³)	$\chi \times 10^6$ (bar ⁻¹)	$a(0)$	γ	η	$g(\sigma)$
0.001	25	0.997 075	45.65	0.062 650	1.066 84	0.348 331	3.093 70
0.001	71	0.977 219	45.65	0.070 876	1.076 28	0.333 728	2.910 97
0.506 7	25	1.018 8	39.91	0.055 966	1.059 28	0.361 541	3.273 36
11.03	25	1.263 9	12.36	0.021 502	1.021 97	0.467 364	5.432 66

($45.65 \times 10^{-6} \text{ bar}^{-1}$) and by Kell ($45.24 \times 10^{-6} \text{ bar}^{-1}$). Being forced to use G. L.'s data as the only reliable source of information on the pressure dependence of ρ at 25 °C, we must consistently normalize Kell's compressibility data to G. L.'s value at 25 °C. Under these circumstances, the most obvious temperature choice is 71 °C, to which we assign, in agreement with Kell's result ($\chi = 45.23 \times 10^{-6} \text{ bar}^{-1}$) the same compressibility as to 25 °C.

The reliability of the P. Y. theory for water is warranted by the hard sphere diameters corresponding to the packing fractions η listed in table I. The resulting values of σ^* at 25 °C range between 2.712 Å (atmospheric pressure) and 2.764 Å (11.03 kbar). Such values are quite reasonable, being slightly higher than the diameter of the oxygen ion (2.64 Å) and lower than the mean distance (2.92 Å) at which one observes experimentally the first peak in the molecular radial distribution [22, 23].

We will now determine the three constants α_0 , A^* and C^* by fitting eq. (20) to the polarizabilities corresponding to the following refractive indices for the sodium D-line ($\lambda = 5893 \text{ Å}$) :

$$\begin{aligned} n_{0.001 \text{ kbar}}^{25^\circ\text{C}} &= 1.33287; & n_{0.001 \text{ kbar}}^{71^\circ\text{C}} &= 1.32524; \\ n_{0.5067 \text{ kbar}}^{25^\circ\text{C}} &= 1.3398. \end{aligned} \quad (24)$$

The two values at 0.001 kbar are taken from Ref. [20], section E-223 (2). The value at 500 atm. (0.5067 kbar) could be directly read on an enlarged photograph of the diagram published by V. L. [1]. This procedure is however not advisable for water, because here the low pressure refractive index data of Rosen [24] are available. As these were found by V. L. themselves to be in excellent agreement with their own results, we adopt for the sodium D-line at 0.5067 kbar the result of the parabolic extrapolation of the three isobaric values of n listed in Ref. [24], namely 1.3401 ($\lambda = 579 \mu\text{m}$), 1.3413 ($\lambda = 546 \mu\text{m}$), 1.3472 ($\lambda = 436 \mu\text{m}$). In this way we obtain the value (1.3398) given by eqs. (24) : the corresponding change $\Delta n = 0.693$ is seen to be consistent with the V. L. diagram.

Table II gives the polarizabilities referring to the three refractive indices (24), according to the various theories examined in section 2. Also shown are the resulting values of the constants α_0 , A^* , C^* .

The first row of table III shows the ideal gas refractive index n^* as obtained by introducing into eq. (22) the polarizabilities α_0 listed in table II. The theoretical values of $(n^* - 1) \times 10^6$ are compared with the experimental results, which are [25] 254 (Fizeau), 257.9 (Jamin), 257 (Mascart), 250 (Lorenz), 255.9 (Wüst and Reindel) and 246.5 (Newbound [26]).

The second row lists the change of refractive index at 11.03 kbar with respect to the reference value at atmospheric pressure (25 °C). The theoretical values of Δn according to the various theories discussed in section 2 are obtained by direct substitution of eq. (20) into eqs. (1)-(6). The result referring to the empirical formula involving the Lagrangian strain, namely [1]

$$\Delta n = \text{const.} \times |\mathcal{E}| \left(3\mathcal{E} + \frac{3}{2}\mathcal{E}^2 = \frac{\Delta V}{V_0} \right) \quad (25)$$

is derived by fitting eq. (25) to the value of Δn at 0.5067 kbar. The experimental result at 11.03 kbar is taken from V. L. [1].

We will not discuss the optical behaviour of water in terms of the high pressure density data of Bridg-

(2) Our values of n_0 (the absolute refractive index at atmospheric pressure, corresponding to the temperature of the V. L.'s experiments) are taken from the most reliable sources available in the literature : they turn out to be slightly different ($\delta n_0 \approx 10^{-4}$) from those introduced by V. L. in the formula

$$\Delta n = \frac{p' \lambda - 2 n_0 \Delta t}{2 t_0}$$

where Δn is the change in the absolute refractive index at the wavelength λ , p' is the total number of fringes shifted, and t_0 and Δt are the initial thickness and the change in thickness, respectively, of the vitreous silica spacer of the interferometer. The discrepancy between the present values of n_0 and those of V. L. does not appreciably affect Δn , as from the above equation $\delta(\Delta n) = \delta n_0 \Delta t / t_0 \approx 10^{-4} \Delta t / t_0$: since $\Delta t / t_0 < 10^{-1}$, we see that $\delta(\Delta n)$ is at least one order of magnitude lower than the uncertainties corresponding to V. L.'s data of Δn .

TABLE II

1st, 2nd and 3rd row : molecular polarizabilities for water ($\lambda = 5893 \text{ Å}$), corresponding to the refractive indices (24) ; 4th, 5th and 6th row : values of α_0 , A^* and C^* , as resulting from direct substitution of the previous polarizabilities into eq. (20).

	Author	Lorentz-Lorenz	F. Brown ($\eta = 1/8 \gamma$)	F. Brown ($\eta = \eta_{P.Y.}$)	Onsager B. ($\eta = \eta_{P.Y.}$)
$10^{24} \alpha_{0.001 \text{ kbar}}^{25^\circ\text{C}} (\text{cm}^3)$	1.503 34	1.472 21	1.404 45	1.486 15	1.301 44
$10^{24} \alpha_{0.001 \text{ kbar}}^{71^\circ\text{C}} (\text{cm}^3)$	1.499 95	1.470 79	1.404 71	1.482 20	1.296 16
$10^{24} \alpha_{0.5067 \text{ kbar}}^{25^\circ\text{C}} (\text{cm}^3)$	1.500 73	1.467 98	1.398 88	1.484 19	1.301 21
$10^{24} \alpha_0 (\text{cm}^3)$	1.509 67	1.562 50	1.565 18	1.463 31	1.204 14
$10^{26} A^* (\text{cm}^6 \cdot \text{g}^{-1})$	3.544	— 5.231	— 12.626	6.444	13.731
$10^{29} C^* (\text{cm}^6 \cdot \text{g}^{-1} \cdot \text{K}^{-1})$	4.530	4.146	3.789	4.503	4.306

TABLE III

1st row : refractive index n^* for an ideal gas of water molecules at 0 °C, 760 mmHg ($\lambda = 5\,893\text{ Å}$) ;
 2nd row : change of absolute refractive index for water at 11.03 kbar with respect to the value at atmospheric pressure (25 °C, $5\,893\text{ Å}$).

	Author	Lorentz- Lorenz	F. Brown ($\eta = 1/8\ \gamma$)	F. Brown ($\eta = \eta_{P.Y.}$)	Onsager B. ($\eta = \eta_{P.Y.}$)	Lagr. strain	Exper.
$(n^* - 1) \times 10^6$	254.9	263.8	264.3	247.1	203.3	—	$246.5 \div 257.9$
$(\Delta n)_{11.03\text{ kbar}}^{25^\circ\text{C}}$	8.23	8.12	8.22	8.23	9.14	7.10	8.21

man [27], reported in section 2-152 of Ref. [28]. These data are certainly affected by some systematic error, as shown by the low compressibility value at atmospheric pressure and 25 °C ($\chi = 41.5 \times 10^{-6}\text{ bar}^{-1}$) which is obtainable by interpolating through Tait's equation the density values at 1, 500 and 1 000 kg/cm².

4.2 N-HEXANE. — By fitting Tait's eq. (23) to Mopsik's data at 25 °C [29] (see also Ref. [30], p. 635)

$$\rho_{0.001\text{ kbar}} = 0.654\,7; \quad \rho_{1.014\text{ kbar}} = 0.724\,0;$$

$$\rho_{2.028\text{ kbar}} = 0.762\,7 \quad (\text{g/cm}^3)$$

we obtain $C = 0.211\,515$; $B = 0.551\,08\text{ kbar}$. Eq. (23) is then extrapolated up to 11.66 kbar, i.e. the maximum pressure reached by V. L. [2] and gives the results shown in table IV.

By parabolic interpolation of Mopsik's isobaric data at -25 °C , 0 °C , 25 °C , we obtain at 20 °C

$$\rho_{0.001\text{ kbar}} = 0.659\,2; \quad \rho_{1.014\text{ kbar}} = 0.726\,8;$$

$$\rho_{2.028\text{ kbar}} = 0.764\,8 \quad (\text{g/cm}^3)$$

and the corresponding Tait's equation with $C = 0.209\,567$, $B = 0.568\,56\text{ kbar}$. These values are sufficient to explain the row referring to 20 °C in table IV.

The hard core diameters corresponding to the values of η listed in table IV (ranging from 5.627 Å at atmospheric pressure up to 5.795 Å at 11.66 kbar, at 25 °C), cannot be compared with any experimental indication, because for n-hexane, to the author's knowledge, no molecular radial distribution function has been determined.

The three constants α_0 , A^* and C^* required by eq. (20) will be now determined by fitting eq. (20) to

the polarizabilities corresponding to the three following refractive indices for $\lambda = 5\,461\text{ Å}$:

$$n_{0.001\text{ kbar}}^{25^\circ\text{C}} = 1.374\,26; \quad n_{0.001\text{ kbar}}^{20^\circ\text{C}} = 1.376\,98;$$

$$n_{1.014\text{ kbar}}^{25^\circ\text{C}} = 1.415\,26. \quad (26)$$

The two values at atmospheric pressure are derived from parabolic interpolation at the required wavelength of the data of Wibaut *et al.* [31] at $6\,563\text{ Å}$, $5\,875.6\text{ Å}$, $4\,861\text{ Å}$, and subsequent multiplication by 1.000 27 (the corresponding absolute refractive index of air at room temperature). The value at 25 °C , 1.014 kbar , reflects a direct reading of the value of Δn (4.10×10^{-2}) on an enlarged photograph of the diagram published by V. L. [2].

Table V shows the polarizabilities corresponding to the three refractive indices (26), as obtained by solving eqs. (1)-(6) with respect to Z . It gives also the resulting values of α_0 , A^* and C^* .

The first row of table VI gives the ideal gas refractive index n^* , deducible from eq. (22) by the values of α_0 listed in table V. The experimental value is deduced from the result 1.002 032 (Ref. [32], 6-876) obtained at $\lambda = 5\,893\text{ Å}$ by Berl and Ranis [33], for the real vapour at 0 °C and 760 mmHg. The van der Waals equation (with $a = 24.39\text{ (liter)}^2 \times \text{atm.} \times (\text{mole})^{-2}$, $b = 0.173\,5\text{ liter} \times (\text{mole})^{-1}$, see Ref. [20], D-178) assigns to one mole of this vapour the volume 21.445 liters, so that from eq. (21)

$$(\alpha_0)_{5893\text{ Å}} = 11.511\,6 \times 10^{-24}\text{ cm}^3.$$

The value of α_0 for $\lambda = 5\,461\text{ Å}$ (required by table VI) is deduced using the reasonable assumption that the ratio of the polarizabilities at two given wavelengths is the same in the liquid and in the vapour phase.

TABLE IV

Density and compressibility data for n-hexane

P (kbar)	t (°C)	ρ (g.cm ⁻³)	$\chi \times 10^6$ (bar ⁻¹)	$a(0)$	γ	η	$g(\sigma)$
0.001	25	0.654 7	166.39	0.031 349	1.032 36	0.427 044	4.423 80
0.001	20	0.659 2	159.80	0.029 806	1.030 72	0.432 552	4.545 28
1.014	25	0.724 0	64.91	0.013 524	1.013 71	0.514 294	7.060 18
11.66	25	0.914 9	10.51	0.002 767	1.002 77	0.651 882	18.496 10

TABLE V

1st, 2nd and 3rd row : molecular polarizabilities for n-hexane ($\lambda = 5\,461\text{ \AA}$), corresponding to the refractive indices (26) ; 4th, 5th and 6th row : values of α_0 , A^* and C^* , as resulting from direct substitution of the previous polarizabilities into eq. (20).

	Author	Lorentz-Lorenz	F. Brown ($\eta = 1/8\ \gamma$)	F. Brown ($\eta = \eta_{P.Y.}$)	Onsager B. ($\eta = \eta_{P.Y.}$)
$10^{24}\ \alpha_{0.001}^{25^\circ\text{C}}\text{ kbar}\ (\text{cm}^3)$	12.248 8	11.917 7	11.288 3	12.145 2	10.697 6
$10^{24}\ \alpha_{0.001}^{20^\circ\text{C}}\text{ kbar}\ (\text{cm}^3)$	12.249 1	11.913 1	11.278 3	12.148 7	10.705 2
$10^{24}\ \alpha_{1.014}^{25^\circ\text{C}}\text{ kbar}\ (\text{cm}^3)$	12.217 5	11.816 5	11.102 7	12.171 8	10.793 1
$10^{24}\ \alpha_0\ (\text{cm}^3)$	12.097 6	12.496 0	12.648 6	11.554 2	9.527 4
$10^{26}\ A^*\ (\text{cm}^6\cdot\text{g}^{-1})$	34.061	— 79.068	— 198.123	98.598	185.32
$10^{29}\ C^*\ (\text{cm}^6\cdot\text{g}^{-1}\cdot\text{K}^{-1})$	8.313	7.026	7.313	6.318	4.985

TABLE VI

1st row : refractive index n^* for an ideal gas of n-hexane molecules at 0°C , 760 mmHg ($\lambda = 5\,461\text{ \AA}$) ;
2nd row : change of absolute refractive index for n-hexane at 11.66 kbar with respect to the value at atmospheric pressure (25°C , $5\,461\text{ \AA}$).

	Author	Lorentz-Lorenz	F. Brown ($\eta = 1/8\ \gamma$)	F. Brown ($\eta = \eta_{P.Y.}$)	Onsager B. ($\eta = \eta_{P.Y.}$)	Lagr. strain	Exper.
$(n^* - 1) \times 10^6$	2 042	2 110	2 136	1 951	1 609	—	1 952
$(\Delta n)_{11.66\text{ kbar}}^{25^\circ\text{C}}$	15.08	14.97	15.02	15.23	17.47	12.61	15.66

This ratio can be obtained therefore by applying eq. (6) to the two refractive indices at 25°C in the liquid phase, namely 1.374 26 ($\lambda = 5\,461\text{ \AA}$) and 1.372 60 ($\lambda = 5\,893\text{ \AA}$). In this way, we find

$$(\alpha_0)_{5461\text{ \AA}} = 1.004\,157\,(\alpha_0)_{5893\text{ \AA}},$$

from which the experimental result of n^* quoted in table VI is immediately deduced.

The theoretical deviations (Δn) at 11.66 kbar with respect to the refractive index at atmospheric pressure are compared in the second row of table VI with the experimental value quoted by V. L. [2].

The figure in the column « Lagrangian strain » is obtained by fitting eq. (25) to the value of Δn at 1.014 kbar (i.e. $\Delta n = 4.10 \times 10^{-2}$).

4.3 N-PENTANE. — According to Landolt-Börnstein (L. B.) [30] (p. 634), the only information on $\rho(P)$ for this liquid comes from Bridgman's old measu-

rements [34, 35]. The values of ρ at 30°C and 15°C listed in table VII are obtained by parabolic interpolation of the three isobaric values at 0°C , 50°C , 95°C which can be deduced from the table of volume changes appearing in L. B., and based on Bridgman's data. The absolute value of ρ at 0°C and 1 atm. ($0.645\,39\text{ g/cm}^3$) required to convert into density values the L. B. table, is taken from Ref. [30], p. 633 and comes from Bridgman [34]. The values of χ at atmospheric pressure and 1.013 kbar derive from Tait's equation fitted to the three densities at 0.001, 1.013 and 3.040 kbar : these are (in g/cm^3) 0.616 5, 0.698 4, 0.771 8, respectively, at 30°C , and 0.631 3, 0.707 0, 0.778 1, respectively, at 15°C .

The value of χ at 10.133 kbar is obtained by a graphical method using the density at 6.08 kbar, which from the L. B. table turns out to be $0.833\,3\text{ g/cm}^3$ at 30°C .

The hard core diameters corresponding to the

TABLE VII

Density and compressibility data for n-pentane

P (kbar)	t ($^\circ\text{C}$)	ρ ($\text{g}\cdot\text{cm}^{-3}$)	$\chi \times 10^6$ (bar^{-1})	$a(0)$	γ	η	$g(\sigma)$
0.001	30	0.616 5	228.74	0.049 280	1.051 83	0.376 264	3.491 53
0.001	15	0.631 3	195.22	0.040 937	1.042 68	0.397 391	3.842 18
1.013	30	0.698 4	75.39	0.018 400	1.018 75	0.483 468	5.926 14
10.13	30	0.888 3	13.50	0.004 191	1.004 21	0.619 292	14.248 73

values of η appearing in table VII range (at 30 °C) between 5.188 Å (atmospheric pressure) and 5.423 Å (10.133 kbar). As for n-hexane, there are no experimental indications to which they could be compared.

The three constants α_0 , A^* and C^* are now determined by fitting eq. (20) to the three polarizability values corresponding to the following refractive indices ($\lambda = 5\,461\text{ Å}$)

$$\begin{aligned} n_{0,001\text{ kbar}}^{30^\circ\text{C}} &= 1.353\,77; \quad n_{0,001\text{ kbar}}^{15^\circ\text{C}} = 1.362\,50; \\ n_{1,013\text{ kbar}}^{30^\circ\text{C}} &= 1.401\,27. \end{aligned} \tag{27}$$

These are derived from the data obtained by Wibaut *et al.* [31]. More precisely, the second value (27) follows from parabolic interpolation at $\lambda = 5\,461\text{ Å}$ of Wibaut's data at 15 °C and subsequent multiplication by 1.000 27, the corresponding absolute refractive index of air. In the same way one gets the value at 20 °C, 0.001 kbar, which turns out to be $1.359\,22 \times 1.000\,27 = 1.359\,59$. By these two refractive indices, and assuming a linear temperature dependence of n , one arrives at the first value (27). The third value (27) comes from a direct reading of $\Delta n (= 4.75 \times 10^{-2})$ on an enlarged photograph of the diagram published by V. L. [2].

In table VIII we list the polarizabilities obtained by inserting the three values (27) into eqs. (1)-(6) : also shown are the resulting constants α_0 , A^* and C^* .

The theoretical values of the ideal gas refractive index n^* , as given by eq. (22), are listed in the first row of table IX : they are compared with the experimental

result of Lowery and Hartley [36] (see Ref. [32], 6-876). In the second row of table IX we list the change of refractive index at 10.133 kbar (i.e. the maximum pressure reached by Bridgman) with respect to the value at atmospheric pressure. The value of Δn in the column « Lagrangian strain » is obtained by fitting eq. (25) to the value at 1.013 kbar (4.75×10^{-2}). The experimental result at 10.133 kbar is read on the enlarged photograph of the V. L. diagram [2].

4.4 CARBON TETRACHLORIDE. — All the values appearing without an asterisk in table X are taken from Mopsik [37] : at 50 °C, the atmospheric pressure compressibility is simply obtained from Mopsik's density value at 0.102 kbar ($1.554\,7\text{ g/cm}^3$), i.e.

$$\chi = \frac{1.554\,7 - 1.535\,8}{1.535\,8 \times 0.101} \times 10^{-3} = 106.41 \times 10^{-6} (\text{bar})^{-1}.$$

At 25 °C the pressure dependence of ρ is described by a Tait's equation fitted to Mopsik's densities at 0.001, 0.609, 1.217 kbar, i.e. $1.584\,7$, $1.666\,8$, $1.725\,2\text{ g/cm}^3$, respectively. In this way one gets $C = 0.217\,014$; $B = 0.884\,72\text{ kbar}$, from which both the density and the compressibility value at 25 °C without asterisk are easily derived.

For the sake of completeness, it is interesting to take the pressure dependence of density from another source, namely the G. L.'s paper [19], where the two constants appearing in Tait's equation are given as follows : $C = 0.212\,9$; $B = 0.867\,0\text{ kbar}$ at 25 °C, and $B = 0.707\,75\text{ kbar}$ (interpolated) at 50 °C.

TABLE VIII

1st, 2nd and 3rd row : molecular polarizabilities for n-pentane ($\lambda = 5\,461\text{ Å}$), corresponding to the refractive indices (27) ; 4th, 5th and 6th row : values of α_0 , A^* and C^* , as resulting from direct substitution of the previous polarizabilities into eq. (20).

	Author	Lorentz-Lorenz	F. Brown ($\eta = 1/8\,\gamma$)	F. Brown ($\eta = \eta_{P.Y.}$)	Onsager B. ($\eta = \eta_{P.Y.}$)
$10^{24} \alpha_{0,001\text{ kbar}}^{30^\circ\text{C}} (\text{cm}^3)$	10.318 9	10.075 2	9.574 4	10.208 5	8.927 4
$10^{24} \alpha_{0,001\text{ kbar}}^{15^\circ\text{C}} (\text{cm}^3)$	10.315 9	10.056 9	9.544 2	10.214 7	8 960 3
$10^{24} \alpha_{1,013\text{ kbar}}^{30^\circ\text{C}} (\text{cm}^3)$	10.269 0	9.951 6	9.377 2	10 212 0	9.033 9
$10^{24} \alpha_0 (\text{cm}^3)$	10.320 5	10 754 8	10.721 0	9.836 1	7.277 0
$10^{26} A^* (\text{cm}^6 \cdot \text{g}^{-1})$	9.943	— 103.386	— 176.761	69.847	290.859
$10^{29} C^* (\text{cm}^6 \cdot \text{g}^{-1} \cdot \text{K}^{-1})$	9.640	6.465	8.708	8.919	21.874

TABLE IX

1st row : refractive index for an ideal gas of n-pentane molecules at 0 °C, 760 mmHg ($\lambda = 5\,461\text{ Å}$) ;
2nd row : change of absolute refractive index for n-pentane at 10.133 kbar with respect to the value at atmospheric pressure (30 °C, $5\,461\text{ Å}$).

	Author	Lorentz-Lorenz	F. Brown ($\eta = 1/8\,\gamma$)	F. Brown ($\eta = \eta_{P.Y.}$)	Onsager B. ($\eta = \eta_{P.Y.}$)	Lagr. strain	Exper.
$(n^* - 1) \times 10^6$	1 743	1 816	1 810	1 661	1 229	—	1 684
$(\Delta n)_{10,133\text{ kbar}}^{30^\circ\text{C}}$	15.45	15.39	15.38	15.51	16.79	12.84	15.70

TABLE X

Density and compressibility data for carbon tetrachloride.

With and without asterisk we list the values coming from G. L. [19] and from Mopsik [37], respectively

P (kbar)	t (°C)	ρ (g.cm ⁻³)	$\chi \times 10^6$ (bar ⁻¹)	$a(0)$	γ	η	$g(\sigma)$
0.001	25	1.584 7	106.41	0.027 181	1.027 94	0.442 522	4.777 35
		1.584 58 *	106.52 *	0.027 207 *	1.027 97 *	0.442 418 *	4.774 85 *
0.001	50	1.535 8	121.84	0.032 692	1.033 80	0.422 445	4.325 83
		1.535 46 *	130.46 *	0.034 997 *	1.036 27 *	0.414 922 *	4.172 02 *
1.94	25	1.779 2	37.46	0.010 743	1.010 86	0.536 473	8.070 06
		1.777 47 *	36.95 *	0.010 587 *	1.010 70 *	0.537 859 *	8.139 63 *

All the values derived from G. L. are marked by an asterisk in table X. Mopsik's density values are always slightly higher than those given by G. L. : the discrepancy between the two corresponding values of density at 1.94 kbar results of the order of 1‰.

The hard sphere diameters at 25 °C corresponding to the packing fractions η listed in table X range from 5.15 Å (at atmospheric pressure) up to 5.28 Å (at 1.94 kbar) : these are acceptable effective values, falling just in the middle of the range between 3.95 Å and 6.4 Å, through which the first shell of neighbours is spread according to Gruebel and Clayton's [38] interpretation of the experimental molecular radial distribution function.

The three constants α_0 , A^* and C^* are determined by fitting eq. (20) to the three polarizabilities corresponding to the following refractive indices at 5 461 Å :

$$\begin{aligned} n_{0.001 \text{ kbar}}^{25^\circ\text{C}} &= 1.460 \text{ }_2; & n_{0.001 \text{ kbar}}^{50^\circ\text{C}} &= 1.444 \text{ }_7; \\ n_{1.94 \text{ kbar}}^{25^\circ\text{C}} &= 1.527 \text{ }_2. \end{aligned} \quad (28)$$

The two values at 0.001 kbar are derived from parabolic interpolation at $\lambda = 5461$ Å of Goss [39] data, and subsequent multiplication by 1.000 27, the corresponding absolute refractive index of air at room temperature. The refractive index at 1.94 kbar is obtained from V. L.'s experimental result ($\Delta n = 6.71 \times 10^{-2}$).

Table XI gives the polarizabilities obtained by introducing into eqs. (1)-(6) the refractive indices (28). It also gives the constants α_0 , A^* and C^* , as obtained by inserting into eq. (20) the above values of the polarizability. We list the results referring to G. L.'s and Mopsik's data with and without asterisk, respectively.

Table XII shows the refractive indices n^* , evaluated by inserting into eq. (22) the polarizabilities α_0 given in table XI. The experimental value is taken from Lowery [40] (see Ref. [32], 6-880).

No experimental information on the refractive index at intermediate pressures between 0.001 kbar and 1.94 kbar is available from V. L.'s paper [1] : this

TABLE XI

From 1st to 6th row : molecular polarizabilities for carbon tetrachloride ($\lambda = 5461$ Å), corresponding to the refractive indices (28); from 7th to 12th row : values of α_0 , A^ and C^* , as resulting from direct substitution of the previous polarizabilities into eq. (20). The values with and without asterisk refer to the analogous data of table X, respectively.*

	Author	Lorentz-Lorenz	F. Brown ($\eta = 1/8 \gamma$)	F. Brown ($\eta = \eta_{P.Y.}$)	Onsager B. ($\eta = \eta_{P.Y.}$)
$10^{24} \alpha_{0.001 \text{ kbar}}^{25^\circ\text{C}}$ (cm ³)	10.934 3	10.538 1	9.776 8	10.850 5	9.176 1
	10.935 1 *	10.538 9 *	9.777 5 *	10.851 2 *	9.176 3 *
$10^{24} \alpha_{0.001 \text{ kbar}}^{50^\circ\text{C}}$ (cm ³)	10.934 1	10.561 3	9.829 4	10.833 3	9.160 6
	10.933 8 *	10.563 7 *	9.828 8 *	10.826 8 *	9.124 7 *
$10^{24} \alpha_{1.94 \text{ kbar}}^{25^\circ\text{C}}$ (cm ³)	11.035 8	10.537 1	9.633 8	11.054 2	9.366 3
	11.046 7 *	10.547 3 *	9.643 4 *	11.066 4 *	9.381 2 *
$10^{24} \alpha_0$ (cm ³)	11.011 5	11.365 8	11.536 5	10.405 6	8.780 7
	11.192 7 *	11.636 5 *	11.621 9 *	10.399 9 *	7.518 1 *
$10^{26} A^*$ (cm ⁶ .g ⁻¹)	— 13.925	— 60.436	— 116.991	15.918	13.401
	— 27.671 *	— 80.605 *	— 123.612 *	15.687 *	104.402 *
$10^{29} C^*$ (cm ⁶ .g ⁻¹ .K ⁻¹)	— 6.354	— 5.759	— 4.178	— 8.536	— 8.111
	— 8.017 *	— 7.964 *	— 5.070 *	— 8.987 *	— 0.171 *

TABLE XII

Refractive index n^* for an ideal gas of CCl_4 -molecules at 0 °C, 760 mmHg ($\lambda = 5461 \text{ \AA}$).
The values with and without asterisk refer to the analogous data of table X, respectively

	Author	Lorentz- Lorenz	F. Brown ($\eta = 1/8 \gamma$)	F. Brown ($\eta = \eta_{P.Y.}$)	Onsager B. ($\eta = \eta_{P.Y.}$)	Exper.
$(n^* - 1) \times 10^6$	1 859 1 890 *	1 919 1 965 *	1 948 1 962 *	1 757 1 756 *	1 483 1 269 *	1 800

explains why the theory is not applied to predict the optical behaviour under pressure for this particular liquid.

5. Discussion. — By analysing the results of the previous section, we draw the following conclusions.

5.1 Among all the formulae examined in section 2, only eq. (6) can be consistently applied to all the liquids investigated by V. L. In fact the parameter a of the van der Waals pressure term being a positive quantity, it follows from eqs. (14), (18) and (19) that A^* and C^* must have the same sign (i.e. the sign of $(d \ln \alpha / d \ln V)_0$). Now this condition turns out to be always fulfilled by author's equation, while it is violated by the Lorentz-Lorenz equation and by the Fuller Brown equation (with $\eta = 1/8 \gamma$) for water, n-hexane and n-pentane, by the Fuller Brown equation (with $\eta = \eta_{P.Y.}$) and by the Onsager-Böttcher equation for carbon tetrachloride.

5.2 From the values of C^* obtained in section 4, and from eq. (19), we get for $K | (d \ln \alpha / d \ln V)_0 |$ the results listed in table XIII. Since $| (d \ln \alpha / d \ln V)_0 |$ is presumably of the order of unity (it would be exactly unity if the Mossotti and Thomson models for α were reliable), it follows that the values of table XIII essentially give the molecular compressibility K . These values turn out to be of the order of magnitude of the compressibilities of solids. This is a very reasonable result, as most of the work done in compressing a solid is used to deform the structure of its molecules (whereas in a liquid the work is spent to reduce the intermolecular distances : this explains the much larger values of χ in the liquid phase).

5.3 Eqs. (14), (18) and (19) can be used to check the reliability of the values of A^* obtained in section 4. In principle, by substituting into eq. (14) the relation $A = k_B A^* / C^*$ (implied by eqs. (18) and (19)) we should obtain a value of the van der Waals parameter a comparable with that coming from the equation of state (16). However, this procedure would be possible only if the depth l of the surface layer were exactly known. Now, the only reasonable information we have on l is that it must be of the same order as the intermolecular distances. For this reason it is better to check the theory by inserting into eq. (14) the experimental value of a coming from eq. (16), and consequently determining l/σ through eq. (14) itself, namely

$$\frac{l}{\sigma} = \frac{4 a C^*}{\pi k_B A^* \sigma^3} \simeq \frac{2}{3} \frac{a C^* \rho N}{k_B A^* \eta M} \quad (29)$$

where A^* , C^* are taken from the tables of section 4. If the theory is reliable, the values resulting from eq. (29) must be of the order of some units. Eq. (29) has been deduced from (14) through the approximation $\sigma = \sigma^*$: this is widely justified because the difference between real and effective molecular diameters, as explained in section 3, concerns only their slight pressure dependence, which in the present case is out of consideration. The discussion can be confined to author's equation : in fact we have seen that the other theories predict for some liquids negative values of a , and therefore are automatically unable to give reasonable values of l . Table XIV gives the values of a at atmospheric pressure, derived from the substitution into eq. (16) of the experimental densities n^0 and of the values of η given by eq. (10). The ratios l/σ according to eqs. (6)-(29) are shown in the second row of the

TABLE XIII

Values of $K | (d \ln \alpha / d \ln V)_0 |$ in 10^{-6} bar^{-1} units, according to the various theories.

The values with and without asterisk for carbon tetrachloride refer to the analogous data of table X, respectively

	Author	Lorentz- Lorenz	F. Brown ($\eta = 1/8 \gamma$)	F. Brown ($\eta = \eta_{P.Y.}$)	Onsager B. ($\eta = \eta_{P.Y.}$)
Water	6.50	5.75	5.24	6.67	7.75
n-hexane	7.12	5.83	5.99	5.67	5.42
n-pentane	8.10	5.21	7.05	7.87	26.08
Carbon tetrachloride	10.67 13.25 *	9.37 12.66 *	6.70 8.07 *	15.17 15.98 *	17.09 0.42 *

TABLE XIV

1st row : values of the parameter a at atmospheric pressure, as deduced from eq. (16) ; 2nd row : depth of the surface layer at atmospheric pressure (measured in molecular diameters) according to eqs. (6)-(20). The values with and without asterisk for carbon tetrachloride refer to the analogous data of table X, respectively.

	Water (25 °C)	n-hexane (25 °C)	n-pentane (30 °C)	Carbon tetrachloride (25 °C)
$a \times 10^{36}$ (dyne.cm ⁴)	6.55	76.9	50.8	62.7 62.7*
l/σ	3.87	0.97	3.25	1.94 1.23 *

table : they are exactly of the expected order of magnitude.

The change of l with pressure is linked to the corresponding change of a : in the units of table XIV, a for water at 25 °C goes from 6.55 (atmospheric pressure) to 4.69 (11.03 kbar) : thus an increment of 11 kbar reduces a of about 28 %. According to eq. (14), a corresponding decrease is expected in the value of l , as the much smaller diminution of the real diameter σ (of the order of 1 %, as one could deduce through the equation $\delta\sigma/\sigma = -\frac{1}{3}Kp$) is negligible. Such a decrease of l is quite reasonable, being of the order of magnitude of the reduction of the intermolecular distance (or of the corresponding rise of density, see table I).

The results contained in tables XIII and XIV are a strong support not only to the theory leading to eq. (6), but also to the model of the molecular polarizability developed in section 3.

5.4 Tables III, VI and IX show that the pressure dependence of the refractive index can be explained in terms of the general theory of dielectric liquids. It is not necessary to introduce empirical relations such as that employed by V. L. : apart from the Onsager-Böttcher equation, which confirms its poor reliability as already stressed in ref. [7], all the formulae discussed in this paper provide a better agreement with experiment than the relation involving the Lagrangian strain. The discrepancies between theoretical and experimental values of n in the high pressure limit are confined within the uncertainties affecting the density data. For water, n-hexane and carbon tetrachloride these data have been derived by an extrapolation procedure involving Tait's equation : under these circumstances an error of the order of some parts in a thousand (as required for instance to explain the experimental value of Δn for n-hexane), is certainly expected to affect the density at 11.66 kbar. In order to obtain an order of magnitude of the differences between two independent sources of density data, we can consider Bridgman's measurements on n-hexane. By interpolation at 25 °C of the table given in Ref. [30], p. 636, based on Bridgman's measurements, we obtain, in

arbitrary units, a specific volume 1.032 9 at atmospheric pressure and 0.754 1 at 10.133 kbar. Normalizing the corresponding densities in such a way as to obtain Mopsik's value at 0.001 kbar (0.654 7 g/cm³), we have $\rho = 0.896$ 8 g/cm³ at 10.133 kbar. This differs by about 3 ‰ from the value deducible through Tait's equation fitted to Mopsik's data, i.e. 0.899 5 g/cm³. Similarly, for carbon tetrachloride a discrepancy of the order of 1 ‰ is shown by table X to exist between the two densities deduced from G. L.'s and Mopsik's data, respectively, at 1.94 kbar. We conclude that an uncertainty of some parts in a thousand is at present unavoidable in our knowledge of the high pressure values of ρ , and this is of course reflected in the theoretical refractive indices, which cannot be predicted with a higher degree of accuracy.

5.5 Eqs. (6) and (20) can be used to get the function $\rho(P)$, starting from measurements of refractive index under pressure. For instance, the pressure dependence of density can be described through the usual Tait's equation (23) : the corresponding compressibility is easily found to be $\chi = 0.434$ 29 (ρ/ρ_0) $C/(B + P)$ so that not only ρ , but also $a(0)$, γ , η and $g(\sigma)$ can be expressed in terms of the two parameters B and C . Consequently, these can be determined by fitting through a least squares analysis eq. (6) to the experimental curve $n(P)$. We have in this way the possibility of determining by an optical method the equation of state of a liquid : such a procedure was already proposed by V. L. [1], but of course in connection with their formula based on the Lagrangian strain, which is certainly much less accurate than our eqs. (6)-(20). Since reliable density data of liquids at high pressures are not available (see section 5.4 and also the discussion of MacDonald [41] in a recent review on the experimental equations of state), the above possibility has to be regarded as a non-trivial result of the theory developed in the present paper.

5.6 Among all the formulae discussed in section 2, eqs. (5) (with $\eta = \eta_{p,y}$) and (6) predict the most reasonable values of n^* . The discrepancies between

theory and experiment are explained in terms of the uncertainties affecting both the measurements of n^* ⁽³⁾ and the density values under pressure used in section 4 to deduce n^* . As shown by table XII, remarkable differences in the theoretical values of n^* are possible even by a change of only 1 % in the density data. It should in any case be pointed out, that a fully reliable theoretical determination of n^* (as well as of A^* and C^*) should be made by applying least squares analysis to a set with a *large* number of refractive index data. This is not always possible, owing to the lack of sufficient experimental data at our disposal on the behaviour of n as a function of P and T . The dependence of n on T has in general only been explored in a very limited temperature range. Among the four liquids discussed in this paper, only water has been studied from the optical point of view in the whole temperature range where the liquid phase exists at atmospheric pressure. For this liquid, we can therefore apply least squares analysis to the set of data listed in table XV : they summarize fairly well the whole information we have on the optical behaviour of water. Of course in this way we renounce the use of the theory for *predicting* the high pressure behaviour. We limit our discussion to eq. (6), from which the values of α listed in the above table are derived. The best fit of eq. (20) to these five values of α provides

$$\begin{aligned}\alpha_0 &= 1.483\,24 \times 10^{-24} \text{ cm}^3, \\ A^* &= 7.02 \times 10^{-26} \text{ cm}^6 \text{ g}^{-1}, \\ C^* &= 5.408 \times 10^{-29} \text{ cm}^6 \text{ g}^{-1} \text{ K}^{-1}\end{aligned}$$

(so that $l/\sigma \simeq 2.33$). The refractive index n^* turns out to be 1.000 250 4, slightly lower than the value obtained in section 4. It is closer to the most recent experimental determination of Newbound [26], who found 1.000 246 5.

⁽³⁾ Which may be very large : for instance, in the case of benzene ($\lambda = 5\,893 \text{ \AA}$), the experimental values of n^* range from 1.001 700 to 1.001 823. See Ref. [20], E-224.

5.7 For carbon tetrachloride, all the theories predict negative values of C^* , and, therefore

$$(d \ln \alpha / d \ln V)_0 < 0.$$

This property is clearly in contrast with the simple Mossotti and Thomson models of the molecular polarizability. Its full comprehension would probably require a troublesome quantum mechanical description of the electronic system in the CCl_4 molecule, under the combined action of the local electric field and of the surrounding molecules. Here, we limit the discussion to one point : the fact that the two peaks at 1.81 \AA and 2.92 \AA found by Gruebel and Clayton [38] in the experimental electronic radial distribution function show a strong departure from the condition of uniform electronic density implied by the Mossotti and the Thomson models. It is therefore not surprising that a conclusion ($d \ln \alpha / d \ln V > 0$) based on such unrealistic models is violated. In the meantime, it should be remembered that the CCl_4 -molecule has a marked departure from spherical symmetry. This is suggested by the experimental molecular radial distribution function, showing two peaks at 3.95 \AA and 6.4 \AA , which share the first shell of neighbours [38]. Such a situation may further contribute to invalidate any conclusion based on the simple relation $\alpha = (\sigma/2)^3$, which is derived under the assumption of spherical symmetry.

As shown by table XI, only eqs. (1), (5) (with $\eta = 1/8 \gamma$) and (6) predict for carbon tetrachloride the same (negative) sign for A^* and C^* . However, the Lorentz-Lorenz and the Fuller Brown equations are not fully satisfactory because of the low values of l/σ (~ 0.42 and ~ 0.15 , respectively). We conclude that the most consistent description of the optical properties of this liquid is obtained using equation (6).

6. **Conclusions.** — The results of section 4 justify the possibility of splitting into the following two parts the problem arising in the theory of dielectric liquids :

a) The definition of a parameter α (molecular polarizability) whose dependence on the thermodynamical state of the liquid must be specified ;

TABLE XV

Set of refractive index data ($\lambda = 5\,893 \text{ \AA}$) and density data for water (1st and 2nd row) and corresponding polarizabilities (4th row) deduced through eq. (6). The compressibilities at $25 \text{ }^\circ\text{C}$ and $71 \text{ }^\circ\text{C}$ used to calculate $g(\sigma)$ (3rd row) were taken from table I. At $100 \text{ }^\circ\text{C}$ the value of χ given by Ref. [20], F-5 ($48.90 \times 10^{-6} \text{ bar}^{-1}$) was corrected into $49.34 \times 10^{-6} \text{ bar}^{-1}$ according to the ratio between the two values of χ at $25 \text{ }^\circ\text{C}$, 0.001 kbar taken from G. L. [19] ($45.65 \times 10^{-6} \text{ bar}^{-1}$) and from the above reference ($45.24 \times 10^{-6} \text{ bar}^{-1}$), respectively. The refractive index at $100 \text{ }^\circ\text{C}$ is taken from Ref. [20], section E-223.

	$P = 0.001 \text{ kbar}$ ($25 \text{ }^\circ\text{C}$)	$P = 0.001 \text{ kbar}$ ($71 \text{ }^\circ\text{C}$)	$P = 0.001 \text{ kbar}$ ($100 \text{ }^\circ\text{C}$)	$P = 0.506\,7 \text{ kbar}$ ($25 \text{ }^\circ\text{C}$)	$P = 11.03 \text{ kbar}$ ($25 \text{ }^\circ\text{C}$)
n	1.332 87	1.325 24	1.318 19	1.339 8	1.414 97
$\rho \text{ (g.cm}^{-3}\text{)}$	0.997 075	0.977 219	0.958 384	1.018 8	1.263 9
$g(\sigma)$	3.093 70	2.910 97	2.720 71	3.273 36	5.432 66
$10^{24} \times \alpha \text{ (cm}^3\text{)}$	1.503 337	1.499 950	1.497 130	1.500 726	1.461 195

b) The solution of the many-body-problem concerning a system of particles with polarizability α under the action of an applied electric field.

These two parts reflect two radically different aspects of the theory, as they essentially represent a short wavelength problem, and a long wavelength problem, respectively. In other words, while in *a*) the structure of the liquid in the neighbourhood of a molecule plays a fundamental role, in *b*) the molecules are always considered from sufficiently large distances so as to justify the point dipole approximation for their electric moments. Consequently, in *a*) the $r \rightarrow 0$ part of the pair correlation $g(r)$ is involved, while in *b*) only the long wavelength condition represented by the Ornstein-Zernike theorem (Eq. 8) is really important. Owing to the strongly different natures of the approximations required in the two cases, the pair correlation used in *a*) must not necessarily be the same analytical function employed in *b*). We use in *a*) the P.Y. theory because the hard sphere model is most appropriate to describe the repulsive part of the interaction, which comes into play for $r \rightarrow 0$. On the contrary, the solution to problem *b*) was obtained in Ref. [4] through the use of a pair correlation satisfying eq. (8), but extraneous to P.Y. theory. Actually, the use of the P.Y. pair correlation in this problem would raise insurmountable analytical difficulties.

In this line of attack to the problem of dielectric liquids the present paper appears as a necessary complement of the theory developed in Refs. [4-8]. In fact the model giving the dependence of α on the thermodynamical state of the liquid, as developed in section 3, turns out to be fully consistent with eq. (6) : more precisely, the system of equations (6)-(20) is able to explain the optical properties of all the liquids investigated by V. L. [1, 2]. These results enhance the reliability of all the equations given in the above references. When the permanent dipoles of the molecules are also involved, the only alternative approach to the theory is represented by the Onsager model : now as shown in section 4 both the equations deducible in the framework of this model, namely the Onsager-Böttcher equation and the Lorentz-Lorenz equation (to which formula (3) reduces when Onsager's approximation $\eta = 1$ is introduced) are largely unsatisfactory. Therefore, the use of the theory based on the truncated Fourier expansion of the dipole-dipole interaction appears to be at present, if not the only possible, certainly the most reasonable choice in the field of dielectric liquids.

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Note added in proof. — It is interesting to see how the results of section 4 are modified when use is made

of the Carnahan and Starling (C.S.) equation for the rigid sphere liquid ⁽¹⁾

$$\tilde{P}/(\tilde{n}^0 \kappa_B T) = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 \quad (30)$$

which represents an alternative, and perhaps more refined solution with respect to the P.Y. or Reiss formula adopted in the text. We emphasize that the correlation function $g(v)$ referring to a given thermodynamical state of the liquid in which the molecules have diameter σ^* is, according to the model of section 3, the same as for a liquid of rigid spheres with diameter σ^* . This is a consequence of the fact that the uniform attractive potential does not give rise to any net force on a bulk molecule. Therefore $g(\gamma)$ is provided by the same analytical expression of the rigid sphere liquid, evaluated for

$$\eta = \pi \tilde{n}^0 (\sigma^*)^3 / 6.$$

In particular, owing to eqs. (14') and (30), the result for $g(\sigma^*)$ in the frame of the C.S. formulation is

$$g(\sigma^*) = (4\eta)^{-1} [(1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 - 1] \quad (31)$$

The full self-consistency of the model is achieved via the Ornstein-Zernicke theorem (Eq. (8)), for which the isothermal compressibility χ is entirely determined by the knowledge of $g(\gamma)$: as the latter refers to a liquid of *rigid* spheres, the same must be true for the former. Consequently χ can be evaluated either by inserting into equation (8) the pair correlation $g(\gamma)$ for rigid spheres (if known), or directly deriving equation (30) with respect to \tilde{n}^0 , at $\sigma^* = \text{constant}$ (without this constraint, which reflects the rigid sphere model, the resulting expression of χ would depend on $d\sigma^*/d\tilde{n}^0$, in contrast with equation (8), as $g(\gamma)$ contains σ^* only through the packing fraction η). Of course the two above procedures lead to the same result only if $g(\gamma)$ is the rigorous analytical solution for the rigid sphere liquid : for instance, the well known discrepancy between the so called *pressure* and *compressibility* P.Y. solutions is just a consequence of the approximations inherent in the P.Y. theory. It is plausible that the C.S. formulation represents a step forward with respect to the P.Y. theory, as equation (30) turns out to be almost indistinguishable from the numerical solution of the Monte Carlo method. Therefore we can perhaps use with more confidence, instead of equation (10), the equation for χ immediately deducible from (30), i.e.

$$\tilde{n}^0 \chi \kappa_B T = [1 + 2\eta(4 - \eta)(1 - \eta)^{-4}]^{-1} \quad (32)$$

Making in (30) the substitution $\tilde{P} = P + a(\tilde{n}^0)^2$ and inserting into (32) the experimental isothermal

⁽¹⁾ *J. Chem. Phys.* **51** (1969) 35.

compressibility, we get from (30), (31), (32), the system replacing equations (16), (15) and (10), respectively, of the text. Moreover, from equations (30) and (32) we get, instead of (17),

$$\left[\frac{d}{d\tilde{n}^0} (a\tilde{n}^{0^2}) \right]_T = \tilde{n}^{0^2} \pi \kappa_B T \sigma^{*2} \left(\frac{d\sigma^*}{d\tilde{n}^0} \right)_T \frac{2(1 + \eta) - \eta^2}{(1 - \eta)^4} \quad (33)$$

The author has repeated in this new framework the calculations for all the liquids discussed in section 4. No substantial change is found with respect to the results previously obtained. For instance, in the case of water one gets, from author's equation (6),

$$A^* = 3.448 \times 10^{-26} \text{ cm}^6 \cdot \text{g}^{-1},$$

$$C^* = 4.569 \times 10^{-29} \text{ cm}^6 \cdot \text{g}^{-1} \text{ K}^{-1},$$

$(n^* - 1) \times 10^6 = 255.0$, $(\Delta n)_{11.03 \text{ kbar}}^{25^\circ \text{C}} = 8.23 \times 10^{-2}$. Within the experimental uncertainties, these numbers are the same as those appearing in tables II and III. Finally, from equation (32) σ^* is always found to increase with \tilde{n}^0 : for water at 25°C , one has $\sigma^* = 2.73 \text{ \AA}$ at 1 atm., and $\sigma^* = 2.79$ at 11.03 kbar. Consequently, equation (33) predicts a decrease of $a(\tilde{n}^0)^2$ with volume: this result, which is a well known property of the attractive pressure term for dielectric liquids, is therefore obtained as a natural consequence of the model.

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