Alternative optical equation for dielectric liquids

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A ''statistically permanent'' pair of molecules interacting by dispersion forces, as a unit element of a simple cubic ''crystal'' modeling a nonpolar liquid dielectric at a given thermal state, has been used to explain low and high pressure refractive index n measurements. It has been shown that the equation

$$(\varepsilon-1)\frac{2\varepsilon+1}{9\varepsilon}=c_\lambda r \exp\frac{r^2}{1-T/T_l}$$

[where $\varepsilon\equiv n^2$, $c_\lambda\geq 1$ close to a unity liquid constant for wavelength λ, $r\equiv 4\pi\rho\alpha/3$, ρ is the number density, α is the mean polarizability of a free molecule, T_l is the internal temperature $\equiv a/RV$, a is the van der Waals constant $\equiv(27/64)(RT_c)^2/p_c$, and R is the universal gas constant] is more accurate than any already known optical equation of liquids. The small changes in Lorentz-Lorenz refraction $L\equiv(\varepsilon-1)V/(\varepsilon+2)$ according to $(\partial L/\partial p)_T<0$ and $(\partial L/\partial T)_p>(\partial L/\partial T)_V>0$ are expected and observed in all pressure ranges. The translational fluctuation parameter $\langle x^{-6}\rangle$ of the right order of magnitude is obtained from n. [S1063-651X(99)04710-8]

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I. INTRODUCTION

There is still an extremely large and unexplained discrepancy between theory and experiment on the refractive index of light of dielectric liquids. A good example of this is liquid carbon tetrachloride, with a translational fluctuation parameter

$$\langle x^{-6}\rangle\equiv\rho\int x^{-6}g(x,\rho,T)dV \tag{1}$$

determined from x-ray scattering measurements by Eisenstein [1] to be 6.1×10^{44} cm^{-6} (a comparable result was obtained independently by Bray and Gingrich [2]), i.e., which predominates by two orders of magnitude over the Buckingham-Stephen [3] theoretical value

$$\langle x^{-6}\rangle=\frac{1}{2\alpha^2}\left(\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{r}-1\right) \tag{2}$$

equal to 0.05×10^{44} cm^{-6}. Also, the analysis of the Coumou *et al.* [4] experimental results on thermal properties of n of liquids by Niedrich [5] shows the molecular polarizability α_l to depend not only on density, as suggested by Kirkwood [6] and others [7], but on temperature as well. These are the main reasons to search for a theory that more adequately explains experimental results than those in the literature. Previously, we came to the conclusion that low pressure results of n measurements indicate the equation $(\varepsilon-1)(2\varepsilon+1)/9\varepsilon=c_\lambda r\exp[r^2/(1-T/T_l)]$ to be of the right form. This was recently confirmed [8] to fit Chen and Vedam's [9] high pressure n measurements of carbon disulfide. Here we will present (i) a derivation of our equation from a model of a liquid at a given thermal state as ''statistically permanent'' (SP) pairs of spherical molecules uniformly distributed in

space, (ii) a comparison with experiment for low and high pressure n measurements of nonpolar liquids, and (iii) a comparison with other theories.

II. THEORY FOR MOLECULAR DISPERSION INTERACTION

The known implicit form of the optical equation for a dielectric liquid [6],

$$\varepsilon-1=4\pi\rho\alpha f(\varepsilon,\rho,T), \tag{3}$$

is based on the assumption that n of a liquid, with its fluctuations, can be represented by identical molecules, with the pair radial distribution function $g(x,\rho,T)$ obtained from x-ray or neutron scattering measurements, exposed to the action of a local field with coefficient $f(\varepsilon,\rho,T)$ dependent not only on ε but on ρ and T as well. It should be noted that the assumption of the identity of the molecules determines α to be independent of the thermal state; otherwise, due to thermal fluctuations, molecules could not be treated as identical even at the same state. The most successful explicit equation is that of the Lorentz and Lorenz,

$$\varepsilon-1=3r/(1-r), \tag{4}$$

obtained by using the approximation $f(\varepsilon,\rho,T)=f(\varepsilon)=(\varepsilon+2)/3$; however, this does not reproduce the thermal dependences of n very well. As we will see below, the Kirkwood equation [6]

$$\varepsilon-1=3r[1+(1+\gamma)r], \tag{5}$$

with $\gamma=(1+a/3bRT)rV/b$, is successful in reproducing pressure variations of n (despite the fact that the small constant of molecular anisotropy σ has been neglected); however, it does not well reproduce its temperature variation. There are other equations in the literature that successfully reproduce temperature variations of n, but there is none that

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reproduces well both the pressure and temperature dependences simultaneously. The question arises of whether for Eq. (3), it will be enough to find the local field with another coefficient $f(\varepsilon)$ or whether it must be $f(\varepsilon,\rho)$ or $f(\varepsilon,\rho,T)$. To answer this question, we assume that (i) the molecules of a liquid are physically not identical (despite their chemical identity) and (ii) the coefficient of the local field is $f_l(\varepsilon)$; therefore, instead of Eq. (3) we have

$$\varepsilon - 1 = 4\pi\rho\alpha_l f_l(\varepsilon), \qquad (6)$$

where $\alpha_l (\neq \alpha)$ is the mean molecular polarizability at a given thermal state. The form of Eq. (6) implies that

$$\rho\frac{\partial\varepsilon}{\partial\rho} = \frac{\varepsilon-1}{1 - \dfrac{\varepsilon-1}{f_l}\dfrac{\partial f_l}{\partial\varepsilon}}\left(1 + \frac{\rho}{\alpha_l}\frac{\partial\alpha_l}{\partial\rho}\right); \qquad (7)$$

therefore, an unknown $f_l(\varepsilon)$ may be eliminated:

$$\frac{(\partial n/\partial\rho)_T}{(\partial n/\partial\rho)_p} = \frac{1 + (\rho/\alpha_l)(\partial\alpha_l/\partial\rho)_T}{1 + (\rho/\alpha_l)(\partial\alpha_l/\partial\rho)_p}, \qquad (8)$$

and comparison with the experimental values by Coumou et al. [4],

$$\frac{(\partial n/\partial\rho)_T}{(\partial n/\partial\rho)_p} = \frac{\alpha_p}{\beta_T}\frac{(\partial n/\partial p)_T}{(-\partial n/\partial T)_p} > 1, \qquad (9)$$

leads to the conclusion that α_l must depend not only on ρ but on T as well; finally, Eq. (6) is

$$\varepsilon - 1 = 4\pi\rho\alpha_l(\rho,T)f_l(\varepsilon), \qquad (10)$$

and

$$(\partial\alpha_l/\partial\rho)_T > (\partial\alpha_l/\partial\rho)_p. \qquad (11)$$

This proves that the full thermal dependence must be explicitly included in a solution of Eq. (6) or Eq. (3). Our model of a liquid should certainly satisfy requirements (10) and (11).

The thermal dependence of $\alpha_l(\rho,T)$ in Eq. (10) is mainly due to dispersion interaction, which implies a small increase compared to α, i.e.,

$$\alpha_l = \alpha + \Delta\alpha + \Delta\alpha_\lambda, \qquad (12)$$

where $\Delta\alpha_\lambda$ depends on λ. The relative variation $\partial\alpha_l/\alpha_l$, assumed to be independent of λ, may be approximated by

$$\frac{\partial\alpha_l}{\alpha_l} = \frac{\partial\Delta\alpha}{\alpha}, \qquad (13)$$

therefore,

$$\alpha_l = c_\lambda\alpha\exp(\Delta\alpha/\alpha). \qquad (14)$$

It was shown by Silberstein [10] that the increase of polarizability of an atom in a diatomic molecule with a constant interatomic distance x, in the dipolar approximation, is $\Delta\alpha_{\text{pair}} = 2\alpha^3 x^{-6}$ (also known as the dipole-induced dipole mechanism). The Silberstein approach let us introduce a

model of a liquid in which the change of polarizability in an interacting pair (such pairs are to be uniformly distributed in space) is taken by analogy as

$$\Delta\alpha = 2\alpha^3\langle x^{-6}\rangle, \qquad (15)$$

where, instead of the constant x^{-6} in a diatomic molecule, there is an unknown constant

$$\langle x^{-6}\rangle = \rho\int x^{-6}dV = \frac{1}{2}\left(\frac{4}{3}\pi\right)^2\frac{\rho}{v} \qquad (16)$$

at a given thermal state [related to the tensor of dipolar interaction by $\langle x^{-6}\rangle = (N/2)\langle T_{ik}^2\rangle$], with $v \equiv 4[4\pi(x_0')^3/3]$, and x_0' the radius of a molecule in the SP pair model. In this way single molecules, identical for all thermal states with $g(x,\rho,T)$, are replaced by uniformly distributed SP pairs of model molecules identical only for a given thermal state.

The implicit form of the van der Waals' equation

$$(p + a/V^2)(V - Nv) = RT, \qquad (17)$$

does not agree with experiment for liquids, i.e., v determined from it depends on the full thermal state (despite its theoretical constancy); however, v in Eq. (16) must also depend on the full thermal state; therefore, there is some possibility that values of v in both these equations are approximately equal to one another. For liquid far from its critical temperature, we take the equation

$$(a/V^2)(V - Nv) = RT \qquad (18)$$

as more appropriate than Eq. (17) to determine

$$v = (1 - T/T_l)/\rho. \qquad (19)$$

Then, from Eq. (16),

$$\langle x^{-6}\rangle = \frac{1}{2}\left(\frac{4}{3}\pi\right)^2\frac{\rho^2}{1 - T/T_l}. \qquad (20)$$

From Eq. (15),

$$\frac{\Delta\alpha}{\alpha} = \frac{r^2}{1 - T/T_l}. \qquad (21)$$

Finally, from Eq. (14),

$$\alpha_l = c_\lambda\alpha\exp[r^2/(1 - T/T_l)]. \qquad (22)$$

The last equation fulfills requirement (11).

Besides α_l, coefficient $f_l(\varepsilon)$ is needed to solve Eq. (10). In view of the increase of $\alpha_l(\rho,T)$, due to short range dispersion interaction, the local field should decrease, compared to that of the Lorentz one, as to include long range interaction only. This condition is fulfilled by the Onsager cavity field, i.e.,

$$f_l(\varepsilon) = g \equiv 3\varepsilon/(2\varepsilon + 1). \qquad (23)$$

This concludes our search for an explicit form of Eq. (6) or Eq. (3) with the result

TABLE I. Values of $\rho(\partial\varepsilon/\partial\rho)_T$ for nonpolar liquids.

Liquid	Lorentz [4]	Onsager [19]	Wertheim [20,21]	Kirkwood Eq. (29)	Niedrich Eq. (28)	Expt. [4]
CS_2	2.60	2.54	2.31	2.24	2.38	2.37
Benzene	1.79	1.58	1.69	1.64	1.65	1.655
CCl_4	1.57	1.42	1.7	1.44	1.46	1.455
$C_{16}H_{34}$[a]	1.43			1.45	1.34	1.35
C_6H_{12}[b]	1.39	1.26	1.34	1.31	1.30	1.29
n-decane	1.33	1.24	1.27	1.25	1.25	1.26
n-octane	1.26	1.19	1.21	1.19	1.19	1.18
iso-octane	1.225	1.175		1.17	1.15	1.15
n-hexane	1.15	1.10	1.11	1.10	1.09	1.075

[a]n-hexadecane.
[b]Cyclohexane.

$$(\varepsilon-1)\frac{2\varepsilon+1}{9\varepsilon}=c_\lambda r\exp\left(\frac{r^2}{1-T/T_l}\right); \qquad (24)$$

therefore,

$$\varepsilon=z+(z^2+0.5)^{0.5}, \qquad (25)$$

where

$$z\equiv\frac{1}{4}\left[1+9c_\lambda r\exp\left(\frac{r^2}{1-T/T_l}\right)\right]. \qquad (26)$$

In terms of identical single molecules with $\alpha_l=\alpha$, our approach is numerically equivalent to replacing the Lorentz local field factor by

$$f(\varepsilon,\rho,T)=c_\lambda\frac{3\varepsilon}{2\varepsilon+1}\exp\left(\frac{r^2}{1-T/T_l}\right), \qquad (27)$$

valid for a nonpolar liquid dielectric far from its critical temperature or approximate for a polar dielectric (except for the temperature dependence on n of water [5]).

III. VERIFICATION AND COMPARISONS

A. Low pressure region

The most complete measurements of thermal ε changes at low pressure, made at the Koninklijke Shell Laboratory in Amsterdam by Coumou et al. [4], are taken to verify theoretical predictions (Tables I and II).

For a pressure ε change, Eq. (24) yields

$$\rho\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T=(\varepsilon-1)\frac{2\varepsilon+1}{2\varepsilon+1/\varepsilon}(1+2r^2)$$

$$\cong(\varepsilon-1)\frac{2\varepsilon+1}{\varepsilon+2}\frac{3(\varepsilon^2+2)}{(2\varepsilon+1/\varepsilon)(\varepsilon+2)}, \qquad (28)$$

while, by differentiation of the Kirkwood equation (5), we have obtained

$$\rho\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T=2(\varepsilon-1)-3r\cong(\varepsilon-1)\frac{2\varepsilon+1}{\varepsilon+2}. \qquad (29)$$

Surprisingly, we did not find the last relation in the literature. Equation (29) differs only slightly from Eq. (28), except for carbon disulfide with $n=1.653$ for which there is $\Delta=-5.5\%$ (Table I). Therefore, in both cases there are similar pictures, for small variations of p of $\varepsilon(p)$, contrary to that of $\varepsilon(T)$, for which the modification by Niedrich [11] of van der Waals' equation for liquids ($v\neq$ const) plays a part. There are other theoretical predictions by known authors included in Table I; however, these (and other, one or more parameter, formulas [12]) do not agree with the experiment except for that of Wertheim. For the isotropic part of Rayleigh's light scattering factor there is $R_{is}\sim[\rho(\partial\varepsilon/\partial\rho)_T]^2$; therefore, a very good agreement of Coumou et al.'s [4], is measurements of R_{is} with that obtained by use of Eq. (28) [5] or Eq. (29) is of primary importance for a confirmation of the now generally accepted [13] high value of Rayleigh's light scattering factor.

For a temperature ε change, Eq. (24) yields [14]

TABLE II. Values of $\rho(\partial\varepsilon/\partial\rho)_p$ for nonpolar liquids.

Liquid	Looyenga Eq. (31)	Niedrich Eq. (30)	Expt. [4,22]
CS_2	2.236	2.26	2.24
Benzene	1.612	1.60	1.59
CCl_4	1.426	1.42	1.41
$C_{16}H_{34}$[a]	1.322	1.31	1.295
C_6H_{12}[b]	1.285	1.27	1.27
n-dodecane	1.267	1.26	1.26
n-decane	1.233	1.22	1.22
n-nonane	1.203	1.17	1.21
n-octane	1.174	1.16	1.16
iso-octane	1.147	1.14	1.14
1-hexene	1.134	1.14	1.13
n-heptane	1.133	1.12	1.15
n-hexane	1.081	1.07	1.05
n-pentane	1.019	1.00	1.01

[a]n hexadecane.
[b]Cyclohexane.

TABLE III. High pressure increase $10^2 \Delta n$ for nonpolar liquids. Carbon disulphide ($\gamma = 0.932$, $c_\lambda = 1.040$).

Pressure (kbar)	Kirkwood Eq. (32)	Niedrich Eq. (33)	Expt. [9,17]
0.54	3.15	3.15	3.12
1.15	5.8	5.88	5.87
2.18	9.3	9.5	9.4
3.09	11.75	12.08	11.98
4.26	14.39	14.88	14.80
5.34	16.51	17.16	17.10
6.19	17.99	18.76	18.72
7.14	19.33	20.44	20.44
8.22	21.06	22.13	22.25
9.46	22.73	23.97	24.16
10.86	22.40	25.84	26.18
11.64	25.29	26.84	27.34
12.46	26.18	27.85	28.32

Mesitilene ($\gamma = 0.676$, $c_\lambda = 1.062$)

Pressure	Kirkwood	Niedrich	Expt.
0.34	1.42	1.40	1.38
0.69	2.58	2.55	2.48
1.04	3.56	3.52	3.43
1.37	4.34	4.29	4.21
1.64	4.99	4.94	4.80
2.05	5.75	5.72	5.59
2.27	6.23	6.18	5.99
2.62	6.88	6.83	6.59
3.00	7.60	7.56	7.19
3.27	8.06	8.02	7.60

Benzene ($\gamma = 0.682$, $c_\lambda = 1.064$)

Pressure	Kirkwood	Niedrich	Expt.
0.25	1.21	1.20	1.23
0.37	1.74	1.72	1.72
0.50	2.25	2.23	2.21
0.64	2.79	2.75	2.72
0.80	3.34	3.30	3.24
0.97	3.88	3.85	3.77
1.07	4.17	4.22	4.04

Carbon tetrachloride ($\gamma = 0.644$, $c_\lambda = 1.044$)

Pressure	Kirkwood	Niedrich	Expt.
0.22	1.12	1.12	1.16
0.48	2.20	2.17	2.22
0.74	3.09	3.04	3.11
1.04	4.02	3.96	4.04
1.29	4.73	4.67	4.76
1.57	5.49	5.42	5.42
1.96	6.39	6.32	6.32

TABLE III. (Continued).

n-octane ($\gamma = 0.514$, $c_\lambda = 1.047$)

Pressure	Kirkwood	Niedrich	Expt.
0.46	1.94	1.91	1.97
1.02	3.66	3.60	3.63
1.47	4.76	4.69	4.69
2.03	5.90	5.83	5.80
3.00	7.52	7.43	7.38
3.94	8.72	8.63	8.63
5.12	10.22	10.12	9.94
6.02	11.16	11.08	10.82

$$\rho \left(\frac{\partial \varepsilon}{\partial \rho} \right)_p = (\varepsilon - 1) \frac{2\varepsilon + 1}{2\varepsilon + 1/\varepsilon} \left[1 + 2r^2 - \frac{1}{\alpha_p T_l} \left(\frac{r}{1 - T/T_l} \right)^2 \right]$$

$$\cong (\varepsilon - 1) \frac{2\varepsilon + 1}{2\varepsilon + 1/\varepsilon} \left[1 + 1.57 \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right)^2 \right], \qquad (30)$$

while from Looyenga's [15] equation comes

$$\rho \left(\frac{\partial \varepsilon}{\partial \rho} \right)_p = 3(\varepsilon - \varepsilon^{2/3}). \qquad (31)$$

Both these results agree very well with experiment (Table II). The Kirkwood equation (5) gives $(\partial n / \partial \rho)_p > (\partial n / \partial \rho)_T$ contrary to the experimental data.

From Tables I and II we can see that although there are equations which give correct results for one of the derivatives, only Eq. (24) gives a correct result for both derivatives simultaneously. In our analysis the Omini [16] equation has been omitted because of the difficulty in finding thermal derivatives of α_p and β_T with good enough accuracy; therefore, we cannot exclude the possibility that it can also give good results for both derivatives.

For Lorentz-Lorenz refraction at low pressure, our consideration as well as experiment led us to the conclusion that $(\partial L / \partial p)_T < 0$ and $(\partial L / \partial T)_p > 0$ because $\rho (\partial \varepsilon / \partial \rho)_p < \rho (\partial \varepsilon / \partial \rho)_T < (\varepsilon - 1)(\varepsilon + 2)/3$, and $(\partial L / \partial T)_V > 0$ because $(\partial \varepsilon / \partial T)_V > 0$ [8].

B. High pressure region

The most complete measurements of the high pressure increase $\Delta n(p)$ of liquids, made in the Materials Research Laboratory and the Department of Physics at Pennsylvania State University by Vedam, Limsuwan, and Chen [9,17], are taken to verify theoretical predictions of the original Kirkwood theory (which appears to be much better than Brown's [18] modification with, e.g., 20% maximum deviation for CS_2 [9])

$$\Delta n = \left[1 + (n_0^2 - 1) \frac{1 + (1 + \gamma)r}{1 + (1 + \gamma)r_0} \frac{r}{r_0} \right]^{0.5} - n_0, \qquad (32)$$

and by our theory,

$$\Delta n = [z + (z^2 + 0.5)^{0.5}]^{0.5} - n_0, \qquad (33)$$

given in Table III. The maximum deviations between theory,

TABLE IV. Maximum deviation of $n(p)$ from experiment at high pressure (in percent) for nonpolar liquids [9,17].

Liquid	Eykman	Lorentz-Lorenz	Onsager-Bottcher	Kirkwood Table III	Omini	Niedrich Table III
CS_2	−13.7	+12.2	+5.2	−7.6	−6.7	−1.8
C_9H_{12}[a]	+1.6	+15.3	+7.1	+6.1	+5.5	+5.5
Benzene	−4.1	+11.6	+8.8	+3.2	−2.4	+4.5
CCl_4	−6.9	+8.1	+4.9	−3.5	−6.9	−3.4
n-octane	−4.1	+10.5	+4.4	+3.1	+2.6	−3.0

[a]Mesitilene.

including that specifically tested by the above cited authors, and experiment are listed in Table IV. The Kirkwood, Omini, and Niedrich equations differ only slightly in reproducing the experimental high pressure dependence $\Delta n(p)$ with not more than a 7.6% maximum deviation in the case of the Kirkwood equation and 5.5% in the Niedrich equation. It would be a difficult task to interpret these small deviations at the moment; however, we see surprising similarities in the results of such different approaches. We agree with Chen and Vedam [9] that the effect of molecular anisotropy is at best only 5% of the observed value of Δn; therefore, the role of molecular shape is sometimes overestimated in the literature. We expect no change in the thermal relations of Lorentz-Lorenz refraction attributed to the high pressure region, and the experimental results confirm this expectation.

IV. TRANSLATIONAL FLUCTUATION PARAMETER $\langle X^{-6} \rangle$

To supplement the verification we propose the translational fluctuation parameter [Eq. (1)], determined either from x-ray or neutron scattering measurements, to be compared with its theoretical value from Eqs. (2) and (20), the hard sphere and Lennard-Jones models. The results for liquid CCl_4 presented in Table V show $\langle x^{-6} \rangle$ for our model to be of the right order of magnitude, contrary to that of the Buckingham-Stephen (BS) model. Also, for liquid argon our $\langle x^{-6} \rangle = 4.6 \times 10^{45}$ cm^{-6} [11] is in accordance with the experimental value $\langle x^{-6} \rangle = 4.2 \times 10^{45}$ cm^{-6} [3,24] contrary to the BS value $\langle x^{-6} \rangle = 0.55 \times 10^{45}$ cm^{-6}. In this context the BS theory must be wrong, while $\langle x^{-6} \rangle$, included in our approach in two ways,

$$T/T_l = 1 - r^2/(2\alpha^2 \langle x^{-6} \rangle), \qquad (34)$$

$$(\varepsilon - 1)(2\varepsilon + 1)/9\varepsilon = c_\lambda r \exp(2\alpha^2 \langle x^{-6} \rangle), \qquad (35)$$

in each way agrees with experiment. This is why we are convinced of the correct molecular interpretation of our optical equation of liquids. It would be interesting to investigate the thermal dependence of $\langle x^{-6} \rangle$ from x-ray or neutron scattering measurements; however, this can hardly be done because of the large experimental inaccuracies.

V. CONCLUSIONS

(1) Molecular dispersion interaction is the origin of thermal changes of n in low and high pressure regions.

TABLE V. Values of $\langle x^{-6} \rangle$ (in units of 10^{44} cm^{-6}) for liquid CCl_4.

Buckingham-Stephen	Theory Hard sphere model Eq. (16)[a]	Theory Lennard-Jones model [23]	Niedrich Eq. (20)[b]	Experiment Eisenstein [1][c]
0.05	1.2	2.6	3.8	6.1

[a]With $v = 4u/\rho$ and $u = 0.7$.
[b]$\langle x^{-6} \rangle = 6.1 \times 10^{44}$ cm^{-6} is obtained from Eq.(35) with $c_\lambda \approx 1$.
[c]$\langle x^{-6} \rangle$ is of the same order of magnitude as obtained by Bray and Gingrich [2].

(2) The n value is determined by $\rho\alpha$ and slightly by T/T_l. There is no explicit effect of molecular shape (anisotropy) on n (this is clear when comparing small molecular dimensions with the wavelength of light). An implicit effect of molecular shape may be through ρ.

(3) The value of T/T_l, important for relations among thermal derivatives of n, is connected with $\langle x^{-6} \rangle$.

(4) To our knowledge the only equation to give correct results for all thermal experimental data on n in low and high pressure regions is, as yet, Eq. (24).

(5) $\langle x^{-6} \rangle$ of the right order of magnitude is obtained from n via Eq. (35).

Now we can reply to the doubts of Chen and Vedam [9] as to the density dependence of the molecular polarizability $\alpha_l \equiv 3L/4\pi N$. From Coumou et al.'s [4] measurements as well as from our theory, it seems that α_l decreases with increasing density, showing the same tendency as in solids, i.e.,

$$\frac{\partial \alpha_l}{\partial \rho} = \frac{\alpha_l}{L} \frac{\partial L}{\partial \rho} = \left[\frac{\rho \partial \varepsilon/\partial \rho}{(\varepsilon - 1)(\varepsilon + 2)/3} - 1 \right] \frac{\alpha_l}{\rho} < 0, \qquad (36)$$

since $\rho(\partial \varepsilon/\partial \rho)_p < \rho(\partial \varepsilon/\partial \rho)_T < (\varepsilon - 1)(\varepsilon + 2)/3$ in all pressure ranges. However, we should stress the unclear character of the physical meaning of the polarizability involved, and the uncertainty of the approximation introduced by the use of the radial correlation function $g(x, \rho, T)$ for such molecules to describe a liquid structure. In our opinion, the role of Onsager's cavity size in liquids, presented recently by Luo et al. [25], seems to be overestimated, and the lack of experimental verification of the theory for spherical molecules may bring about some doubts.

Finally, we must note that (i) our equation is not good for liquids for which quantum effects play a role (e.g., neon), and (ii) there are scattered data in the literature which differ from what we could expect from our theory [26]. However, these data are inconsistent with generally accepted experimental values [8].

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