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SOME RECENT RESULTS ABOUT THE DEPOLARIZATION OF THE RAYLEIGH LIGHT SCATTERED BY OPTICALLY ISOTROPIC MOLECULES

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Résumé. — Nous exposons ici quelques résultats concernant des mesures de dépolarisation de la lumière diffusée par l'argon et le méthane gazeux. Cette dépolarisation est l'indice des fluctuations de moments dipolaires. Nous tentons d'expliquer ces fluctuations en les attribuant aux fluctuations de champ polarisant. L'accord est bon pour les corps étudiés. Cependant Buckingham *et al.* [1] ont montré par l'étude de l'effet Kerr qu'une telle interprétation n'était pas valable pour toutes les molécules isotropes.

Abstract. — We give some results of measurements about the depolarization of the light scattered by gaseous Argon and Methane. We try to explain our results by taking into account the fluctuations of the polarizing field. The agreement is rather good for Argon and Methane but the study of the Kerr effect by Buckingham *et al.* [1] indicates that it is not true for all the isotropic molecules.

I. GENERALITY. — The scattering of the incident light by a medium of isotropic molecules is due to the fluctuation of the induced density of polarization; in the Brillouin-Rayleigh scattering the fluctuations of individual dipolar moments are negligible; the main effect is due to the fluctuations of density which modify the number of molecules in a given volume, so its total dipolar moment. This mechanism can't explain the depolarization which is related to the fluctuations of orientation of the density of polarization, thus to the fluctuations of molecular dipolar moments. It is known that the dipolar moment is the product of the polarizability by the polarizing field. Those two terms can fluctuate and two extreme mechanisms may be used to explain the depolarization.

1. The depolarization is mainly connected to the fluctuations of the polarizing field. This theory was first given by Yvon [2] and modified by Fixman [3]. It was used by many authors [4]-[13].

2. On the other hand the depolarization is due to the fluctuations of polarizability. This theory was first given by Levine and Birnbaum [14] and used by several authors [15].

In fact, it's an easy but rough classification: when a pair of molecules collides, its dipolar moment fluctuates and we can define the polarizability of the pair, but not the polarizability of each molecule. However, the different authors often choose the type of interpretation directly, or when they use a kind of physical data.

Moreover an important result is given by Mazur, Mandel and Jansen [16]-[19]: if we neglect the effect of overlapping of the electronic wave functions of

two molecules, we can attribute the fluctuations of orientation of the density of polarization mainly to the fluctuations of field. It indicates that the long range effects are due to the fluctuations of field, but there are few calculations for the short range effects. In this paper our theoretical calculations are made by using a theory of fluctuation of field. We expound first the experimental results, and give our interpretation in a second part.

II. EXPERIMENTAL RESULTS. — **II.1 Scheme of the apparatus.** — A linearly polarized beam of exciting laser light travels through a high pressure cell which can be filled by gaseous Argon or Methane; we can rotate its plane of polarization with the aid of a half-wave plate. We give two orientations to the exciting field (vertical labelled v or horizontal h). We can analyse the scattered field by using two lens, a Wollaston analyser, a mobile diaphragm and a photomultiplier. Therefore we can select two orientations of the scattered field (vertical V or horizontal H). The scheme of the apparatus is given by the figure 1.

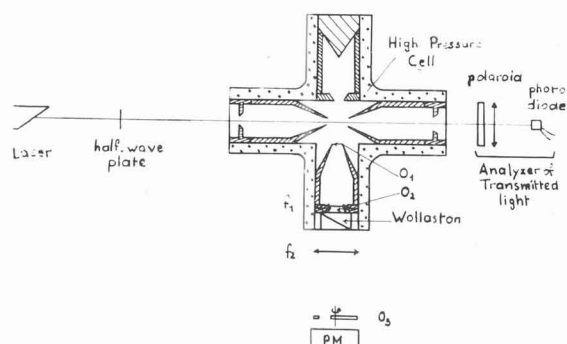


FIG. 1. — Apparatus scheme. Experimental apparatus.

II.2 Definition of the depolarization. — The scattered field is labelled by two letters ; the first one (*V* or *H*) indicates the orientation of the scattered field, the second one (*v* or *h*) gives the orientation of the exciting field. So E_{Vh} indicates a vertical scattered field due to an horizontal exciting field and its intensity is labelled *Vh*. Classically the « polarized » component *Vv* only exists. The other components *Hh*, *Vh*, *Hv* are « depolarized » components. We define a rate of depolarization η by the following ratio :

$$\eta = \frac{Hh + Vh}{Vv + Hv} \tag{1}$$

In this ratio the main part of *Vv* + *Hv* is due to the Brillouin and Rayleigh scattered light, so this ratio allows us to compare the depolarized and the Brillouin-Rayleigh intensities. It's the ratio of the light scattered in the axis of the exciting field and at right angle on this axis. We wanted also to compare *Hh*, *Vh*, *Hv*. The equality *Vh* = *Hv* is well known [20] ; so it's sufficient to study the ratio *Hh/Vv* and *Vh/Vv*.

II.3 Experimental results. — **II.3.1 MEASUREMENTS OF η .** — For Argon at room temperature we have given the value of η versus the density at pressures up to 1 800 bars [10]. We give some results for Methane and Argon at room temperature and low pressure (up to 200 bars). In figure 2, we draw η versus the quantity ξ for Argon and Methane. ξ is defined by the following equation :

$$\xi = \rho \frac{V_m}{RT\chi_T} \left(1 - \frac{\rho}{\rho_0}\right)^2 (1 + \delta) \tag{2}$$

At very low density ξ is equal to the density ρ (ρ is given in Amagat) ; V_m is the volume, R the constant of ideal gas, T the absolute temperature, χ_T the isothermal compressibility, ρ_0 is about the density in liquid state.

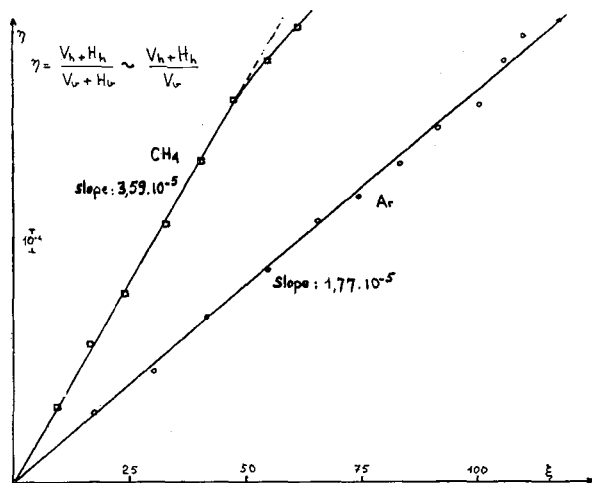


FIG. 2. — Depolarization ratio η versus ξ .

($\rho_0 = 780$ Amagat for Argon, $\rho_0 = 580$ Amagat for Methane). The factor $V_m/RT\chi_T$ [is an interference factor which plays a part in the calculation of the

Brillouin-Rayleigh light, the factor $(1 - \rho/\rho_0)^2$ takes into account the interference effects acting upon the depolarized intensities, δ is a corrective term which is related to the true statistic of pairs.

In fact the used value of η is equal to the experimental value minus η measured at zero density. This last quantity is not exactly equal to zero, because it's due to the finite aperture of the diaphragms : we don't study rigorously the light scattered on the axis of the exciting field. This fact introduces a supplementary measured depolarization which gives a constant contribution to η when the density varies. So, the real value of η at some density is equal to the difference between the measured value at this density and the measured value at zero density. This last value of η is about 1.2×10^{-3} .

We observe that η varies linearly with ξ as predicted by our theory. The slope of the curve is equal to $(1.77 \pm 0.06 \times 10^{-5})$ for Argon, and

$$(3.59 \pm 0.12 \times 10^{-5})$$

for Methane. The value of η is typically equal to some thousandth.

II.3.2 COMPARISON BETWEEN *Hh* AND *Vh*. — The results of measurements of the ratios *Hh/Vv* and *Vh/Vv* are plotted on the figure 3. The origins of each curve have been arbitrarily choosed for convenience. Within the limits of accuracy the two curves are linear with slopes $(0.81 \pm 0.08 \times 10^{-5})$ and

$$0.88 \pm 0,08 \times 10^{-5}.$$

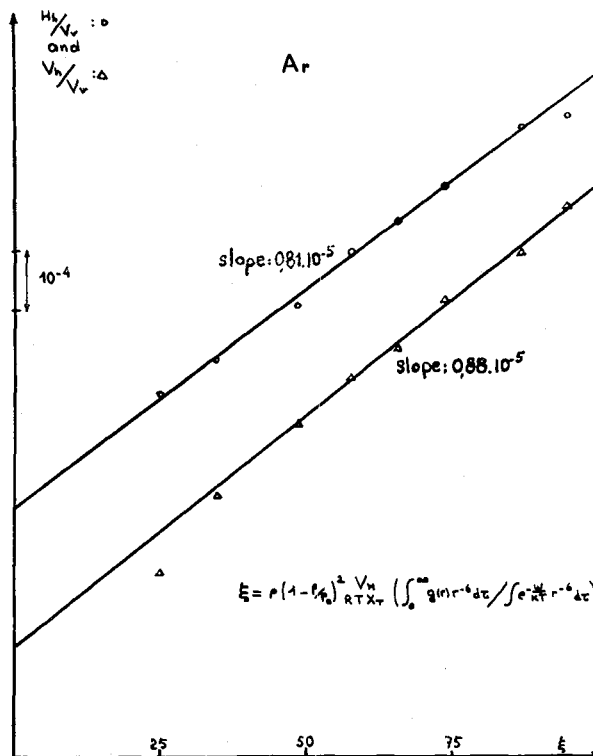


FIG. 3. — Comparison between *Hh* and *Vh*.

In fact, Vh and Vv have the same axial structure but it is not true for Hh and Vv ; so the value 0.88×10^{-5} is more reliable than the value 0.81×10^{-5} .

Moreover the ratio equal to $\frac{Vh}{Vv} + \frac{Hh}{Hv}$ is nearly equal to $\frac{Vh}{Vv} + \frac{Hh}{Vv}$; the value of η/ξ is 1.77×10^{-5} , nearly twice the value of $\frac{Vh}{Vv}/\xi$ (0.88×10^{-5}). It shows that Hh and Vh are equal within the limits of accuracy. This result shows that the range of the perturbation which is at the origin of the depolarized intensities is much smaller than the wavelength of the exciting light. In this case, the fundamental physical data of the incident beam is the orientation of the electrical field, and Hh must be equal to Vv , by reason of symmetry. However the measurements and the connected conclusion are only valid in the range of low densities.

At last a theoretical study of the spectral profile for a low density medium and a experimental test of this calculation have been exposed elsewhere [9], [11].

III. THEORETICAL CALCULATION. — III.1 Fundamental hypothesis and general results. — First of all, we assume that the polarizability of a molecule does not depend on the density, and we use a theory of fluctuation of field introduced by Yvon [2]. The irregularity of the environment of a molecule p induces a fluctuation of the field E_{eff}^p polarizing this molecule.

At the first order of fluctuation, this field can be written :

$$E_{\text{eff}}^p = G^p \left(U + \sum'_q \alpha S^{qp} \right). \quad (3)$$

G^p is the sum of the external field and of the field created by distant molecules. We assume that it does not fluctuate.

— S^{qp} is the tensor describing the field created in p by a dipole put in q .

— α is the polarizability of molecule.

— U is the tensor identity.

— The field $\sum'_q \alpha S^{qp} G^p$ is created by the neighbouring molecules. This vicinity is indicated by the super-script prime. This field is zero in average and represents the fluctuations of field; it connects them with the fluctuations of density, and it is at the origin of the depolarized intensities and of the wings of the polarized intensities.

This calculation is the beginning of an expansion of field in power of αS ; we have used only a calculation of first order.

The dipolar moments induced by the field (3) are responsible for the scattered intensities and so, we obtain the well known formula [2] :

$$\eta = 2 \alpha^2 \frac{V_m}{RT\chi_T} \left\langle \sum'_{q,s} S_{12}^{aq} S_{12}^{st} \right\rangle. \quad (4)$$

S_{12}^{aa} indicates an off-diagonal term of the tensor S^{aa} . The brackets $\langle \rangle$ indicate an average over all the possible microscopic configurations.

We try to evaluate the formula (4) at low and high density.

III.2 Calculations at low density. — At low density two different pairs are not connected, the mean value of S_{12}^{aa} is zero. The non-zero contribution to η is only due to terms where a, q , and s, t represent the same pair ($a = s, q = t$ or $a = t, q = s$); then we obtain the expression :

$$\eta = 4 \alpha^2 \frac{V_m}{RT\chi_T} \left\langle \sum'_q (S_{12}^{aq})^2 \right\rangle \quad (5)$$

where :

$$S_{12}^{aa} = \frac{3}{4 \pi \epsilon_0} \frac{R_1^{aa} R_2^{aa}}{(R^{aa})^2} \frac{1}{(R^{aa})^3}. \quad (6)$$

The subscripts 1, 2, 3 indicate the three basic vectors.

An average on the orientation of the whole medium gives the following formula :

$$\eta = \frac{12}{5} \left(\frac{\alpha}{4 \pi \epsilon_0} \right)^2 \frac{V_m}{RT\chi_T} \left\langle \frac{1}{r^6} \right\rangle \quad (7)$$

where $\langle r^{-6} \rangle$ indicates

$$\left\langle \sum'_q (R^{aq})^{-6} \right\rangle = n \int g(r) r^{-6} 4 \pi r^2 dr$$

n is the numerical density, $g(r)$ the radial distribution function.

We can write the equation (7) in the following way :

$$\eta = Ax \quad (8)$$

when A is a constant :

$$A = \frac{12}{5} \left(\frac{\alpha}{4 \pi \epsilon_0} \right)^2 n_0 \int r^{-6} \exp \left[-\frac{W}{kT} \right] dt \quad (9)$$

— n_0 is the numerical density in S. T. P.

— W is the intermolecular potential.

The variable x is equal to

$$x = \rho \frac{V_m}{RT\chi_T} \frac{\int r^{-6} g(r) dt}{\int r^{-6} \exp \left[-\frac{W}{kT} \right] dt}. \quad (10)$$

At very low density x is equal to ρ , and η is then proportionnal to ρ . This can be understood in the following manner : at low density, the most probable anisotropic group of molecules is the pair; the depolarized intensities are proportionnal to the number of pairs, hence to ρ^2 , while the polarized intensity is proportionnal to the number of molecules, hence to ρ , and the ratio η is proportionnal to ρ .

In fact and even to explain the experimental results at one hundred bars, the hypothesis of the independence

of the orientations of two different pairs is insufficient and we have established with the aid of the vacancy model [8] a formula which takes into account the correlations of orientation :

$$\eta = A\xi$$

where

$$\xi = \left(1 - \frac{\rho}{\rho_0}\right)^2 x \tag{11}$$

ρ_0 is a density, which is near the density of the liquid state : ($\rho_0 = 780$ Amagat for Argon, $\rho_0 = 580$ Amagat for Methane). Experimentally we have observed that η is proportional to ξ .

We may compare the calculated values of η/ξ for a given type of potential and the experimental values of this ratio. For calculations, we use three types of potential :

a) Lennard-Jones potential :

$$W = 4 \varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right].$$

The values of ε and σ are those deduced from the study of the second virial thermodynamical coefficient :

(for Argon $\sigma = 3.405 \text{ \AA}$, $\varepsilon/k = 120 \text{ }^\circ\text{K}$, for methane $\sigma = 3.81 \text{ \AA}$ and $\varepsilon/k = 140 \text{ }^\circ\text{K}$). The respective values of α are 1.63 \AA^3 and 2.60 \AA^3 .

b) Hard core Lennard-Jones potential

$$W = 4 \varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad \text{for } r > \sigma$$

$$W = \infty \quad \text{for } r < \sigma.$$

c) Hard sphere potential :

$$W = \infty \quad \text{for } r < \sigma$$

$$W = 0 \quad \text{for } r > \sigma$$

We use for the three cases the same values of σ and ε . The ratio :

$$\frac{\int r^{-6} g(r) d\tau}{\int r^{-6} \exp\left[-\frac{W}{kT}\right] d\tau}$$

may be written : $(1 + \delta)$; δ is a small correction at low density, so we have calculated it using only a hard sphere potential obtaining :

$$\delta = 24 \pi(1 + 6 \ln 2) n\sigma^3.$$

Then the knowledge of the state equation allows us to determine ξ and η/ξ , we can draw the following table :

Value of η/ξ

Gas	Experimental value	potential a	Theoretical value potential b	potential c
Argon	$(1.77 \pm 0.08) 10^{-5}$	2.65×10^{-5}	2.28×10^{-5}	1.82×10^{-5}
Methane	$(3.59 \pm 0.12) 10^{-5}$	4.82×10^{-5}	4.30×10^{-5}	3.31×10^{-5}

We see that the agreement is rather good for the Hard sphere potential, but not very satisfying for the potential a which is more realistic. It's rather difficult to know the reasons of this discrepancy : this may be due to an insufficiency of the fundamental hypothesis, or the calculations are not sophisticated enough. However the experimental results of the depolarization for argon are in agreement with the measurements of optical Kerr effect made by Buckingham and Dunmur [1]. Gray and Ralph [21] make a rigorous calculation of the first and second term of the virial expansion of η ; they conclude that the theory of field fluctuations is insufficient. We remark that our calculation of η using a crude model (vacancy model) gives a general good agreement. It would be interesting to know the reasons of the discrepancy between the two theories.

III.3 Depolarization at high density. — III.3.1

MAIN FEATURES. — At high density, the molecules can be found into some more symmetrical arrangements than the different pairs. So there are some destructive interferences for the scattered radiation of the different pairs and the formula (7) give results in excess. We plot (Fig. 4) the ratio Y equal to measured

η over $1.77 \times 10^{-5} x$. The value Ax is that predicted by a theory of independant pairs, and the coefficient A

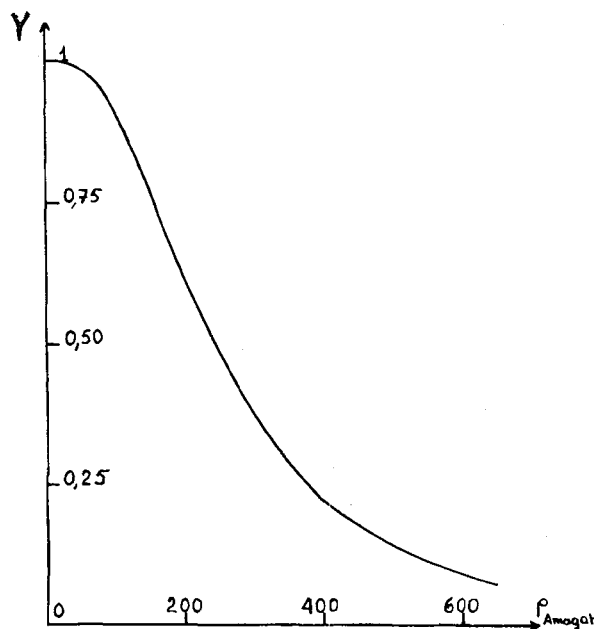


FIG. 4. — Interference factor Y versus the density ρ .

is the measured one. This ratio is equal to one at low density and vanishes at high density. For the calculation of this effect of interference, we use different models of dense medium. The starting point is the following one : at very high density medium, we try to take into account the efficient desordering fluctuations with the aid of models.

III.3.2 MODELS USED AT HIGH DENSITY. — III.3.2.1 *Vacancy model.* — We use in a first time a vacancy model. The possible molecular positions are the sites of a regular lattice. The fluctuations are due to the fact that a site may be occupied or not. Hence, we obtain [8] the formula (7) for the depolarization ratio. The depolarized intensities are zero when all the sites are occupied at the density named ρ_0 .

III.3.2.2 *Cell model.* — A first calculation was made with this model [10]. We give here a more refined calculation. In this model, the fluctuations are due to the displacements of the molecules in their cages. We assume that the displacements in different cells are independent.

III.3.2.3 *General calculations with cell model.* — The value of S^{aa} depends on the displacement of the molecules in their cells (written \mathbf{r}^a and \mathbf{r}^q) and we may write :

$$S_{12}^{aa}(\mathbf{r}^a, \mathbf{r}^q) = y^{aa}(\mathbf{r}^a, \mathbf{r}^q). \quad (12)$$

The functions y^{aa} have the following properties [13] :

$$\overline{y^{aa}(\mathbf{r}^a, \mathbf{r}^q)^a} = y^{aa}(0, \mathbf{r}^q). \quad (13)$$

The upper line indicates an average over the possible displacements in one or two cells. The reference of the cell is given by the letter at the end of this line. The fact that the polarization of the mean polarizing field is well defined may be written :

$$\overline{\sum_q y^{aa}(\mathbf{r}^a, \mathbf{r}^q)^{a,q}} = \sum_q y^{aa}(0, 0) = 0. \quad (14)$$

We assume that the mean field created by the environment on the molecule a is always zero, even if the molecule a is not at the center of the cage :

$$\sum_q \overline{y^{aa}(\mathbf{r}^a, \mathbf{r}^q)^a} = \sum_q y^{aa}(\mathbf{r}^a, 0) = 0. \quad (15)$$

So the mean field created by the environment has the properties of symmetry of the mean field created by a continuous and homogeneous environment.

We have established [10]-[12] the following equations :

$$\eta = 4 \alpha^2 \frac{V_m}{RT\chi_T} \left\langle \sum_q \overline{[y^{aa}(\mathbf{r}^a - \mathbf{r}^q)]^2}^{a,q} - \overline{[y^{aa}(-\mathbf{r}^a)]^2}^a - \overline{[y^{aa}(\mathbf{r}^q)]^2}^q + [y^{aa}(0)]^2 \right\rangle. \quad (16)$$

If we take into account the expression of S_{12}^{aa} and if we calculate the average over all the possible orientations of the whole medium, the value of η becomes :

$$\eta = \frac{12}{5} \left(\frac{\alpha}{4 \pi \epsilon_0} \right)^2 \frac{V_m}{RT\chi_T} B \quad (17)$$

where B is given by the following expression :

$$B = \left\langle \sum_q' | \mathbf{R}_0^{aa} + \mathbf{r}^q - \mathbf{r}^a |^{-6} - | \mathbf{R}_0^{aa} + \mathbf{r}^a |^{-6} - | \mathbf{R}_0^{aa} - \mathbf{r}^a |^{-6} + (R_0^{aa})^{-6} \right\rangle. \quad (18)$$

R_0^{aa} is the distance between the two centers of cells when the molecules a and q move.

\mathbf{r}^a and \mathbf{r}^q play two similar parts and we can write :

$$B = \sum_q' \langle C^{aa}(\mathbf{r}^q - \mathbf{r}^a) - 2 C^{aa}(\mathbf{r}^q) \rangle \quad (19)$$

where C is defined by the following formula :

$$C(\boldsymbol{\beta}) = | \mathbf{R}_0 + \boldsymbol{\beta} |^{-6} - R_0^{-6} \\ = (R_0^2 + \beta^2 - 2 R_0 \beta \cos \theta)^{-3} - R_0^{-6} \quad (20)$$

θ is the angle between \mathbf{R}_0 and $\boldsymbol{\beta}$.

If we assume that the probability density for a molecule to be at a point of the cell is only a function of the distance from the center, we can make an angular average over $C(\boldsymbol{\beta})$, named $\overline{C(\boldsymbol{\beta})}^\Omega$:

$$\overline{C(\boldsymbol{\beta})}^\Omega = \frac{R_0^2 + \beta^2}{(R_0^2 - \beta^2)^4} - \frac{1}{R_0^6}. \quad (21)$$

We deduced from the equations (17), (18), (19), (21) the following value of η :

$$\eta = \frac{12}{5} \left(\frac{\alpha}{4 \pi \epsilon_0} \right)^2 \frac{V_m}{RT\chi_T} \left\langle \sum_q' \frac{(R_0^{aa})^2 + |\mathbf{r}^q - \mathbf{r}^a|^2}{[(R_0^{aa})^2 - |\mathbf{r}^q - \mathbf{r}^a|^2]^4} - 2 \frac{(R_0^{aa})^2 + (r^q)^2}{[(R_0^{aa})^2 - (r^q)^2]^4} + \frac{1}{(R_0^{aa})^6} \right\rangle. \quad (22)$$

We'll first give a general finite expansion of the preceding formula and secondly a rigorous calculation when the probability density is constant in the cell.

The finite expansion of $\overline{C(\boldsymbol{\beta})}^\Omega$ in power of the ratio $z = \beta/R_0$ is given by :

$$\overline{C(\boldsymbol{\beta})}^\Omega = R_0^{-6} [5 z^2 + 14 z^4 + 30 z^6 + 55 z^8 + 0(z^{10})]. \quad (23)$$

Then we can expand the formula (22) ; the averages over the different terms have the following values :

$$\langle (\mathbf{r}^q - \mathbf{r}^a)^u - (\mathbf{r}^q)^u - (\mathbf{r}^a)^u \rangle = I_u. \quad (24)$$

The useful values of I_u are :

$$I_2 = 0, I_4 = \frac{10}{3} \langle r^2 \rangle^2, I_6 = 14 \langle r^2 \rangle \langle r^4 \rangle, \\ I_8 = 24 \langle r^2 \rangle \langle r^6 \rangle + \frac{126}{5} \langle r^4 \rangle^2 \quad (25)$$

where $\langle r^s \rangle$ is defined by the equality :

$$\langle r^s \rangle \equiv \langle (r^a)^s \rangle = \langle (r^q)^s \rangle$$

$\langle r^s \rangle$ indicates an average over all the possible positions in the cells. Then the depolarization ratio is given by :

$$\eta = \left(\frac{\alpha}{4 \pi \epsilon_0} \right)^2 \frac{V_m}{RT \chi_T} \sum_q K^{aq} (R_0^{aq})^{-6} \quad (26)$$

where :

$$K^{aa} = 112 \frac{\langle r^2 \rangle^2}{(R_0^{aa})^4} + 1008 \frac{\langle r^2 \rangle \langle r^4 \rangle}{(R_0^{aa})^6} + 3168 \frac{\langle r^2 \rangle \langle r^6 \rangle}{(R_0^{aa})^8} + 3326,4 \frac{\langle r^4 \rangle^2}{(R_0^{aa})^8} + \dots \quad (27)$$

For the complete calculation, we have to know the distribution of the centers of the cells and the probability density for a molecule to be at a point of the cell. We use the following calculations to evaluate the preceding formula. We assume that the molecules are hard spheres, and that, for crystal structure, we can define the greatest theoretical density ρ_m when the molecules are in contact. At a lower density the centers of the cells define the same crystal structure but the lattice spacing is greater : the distance d between two neighbouring centers is now :

$$d = \sigma \left(\frac{\rho_m}{\rho} \right)^{1/3} \quad (28)$$

The values of the exponent p in the different expression as $\sum (R_0^{ap})^{-p}$ found in (26) are great ($p \geq 10$). Hence, it's sufficient to take into account the most closed cells for which the coordination number v depends only upon the lattice structure, and it can be written :

$$\sum (R_0^{am})^{-p} = v d^{-p} = v \sigma^{-p} \left(\frac{\rho}{\rho_m} \right)^{p/3} \quad (29)$$

B is defined by (17) and we deduce from (22) and (28) :

$$B = \frac{5}{12} \frac{v}{\sigma^6} \left(\frac{\rho}{\rho_m} \right)^2 \left[112 \frac{\langle r^2 \rangle^2}{\sigma^4} \left(\frac{\rho}{\rho_m} \right)^{4/3} + 1008 \frac{\langle r^2 \rangle \langle r^4 \rangle}{\sigma^6} \left(\frac{\rho}{\rho_m} \right)^2 + 3168 \frac{\langle r^2 \rangle \langle r^6 \rangle}{\sigma^8} \left(\frac{\rho}{\rho_m} \right)^{8/3} + 3326,4 \frac{\langle r^4 \rangle^2}{\sigma^8} \left(\frac{\rho}{\rho_m} \right)^{8/3} + \dots \right] \quad (30)$$

This formula gives η if the probability density in a cell is known. Now, we will carry on the calculation in the case where this density is constant.

III.3.3 CASE OF A CONSTANT PROBABILITY DENSITY. — The useful values of $\langle r^s \rangle$ in (25) are easily evaluated and the formulas (17) and (27) become :

$$\eta = \left(\frac{\alpha}{4 \pi \epsilon_0} \right)^2 \frac{V_m}{RT \chi_T} \left(\frac{\rho}{\rho_m} \right)^2 v \left\{ 2,52 \left[\left(\frac{d_c}{\sigma} \right) \left(\frac{\rho}{\rho_m} \right)^{1/3} \right]^4 + 4,05 \left[\left(\frac{d_c}{\sigma} \right) \left(\frac{\rho}{\rho_m} \right)^{1/3} \right]^6 + 4,86 \left[\left(\frac{d_c}{\sigma} \right) \left(\frac{\rho}{\rho_m} \right)^{1/3} \right]^8 + \dots \right\} \quad (31)$$

where d_c is the diameter of the sphere in which the center of the molecule moves. It's connected to the usual diameter of cell D_c by the following equality :

$$D_c = d_c + \sigma \quad (32)$$

III.3.4 RIGOROUS CALCULATION OF THE FORMULA (22) IN THE CASE OF A CONSTANT PROBABILITY DENSITY. — We must calculate the probability to have the following inequality :

$$r + dr > |r^q - r^a| > r \quad (33)$$

We can solve geometrically this problem : we represent the two cells a and q by two spheres of diameter d_c , and their centers O_a and O_q are put to make the equality :

$$O_q O_a = r^q - r^a \quad (34)$$

If a point N is defined by the equality :

$$O_a N = r^a \quad (35)$$

we have :

$$O_q N = r^q \quad (36)$$

So, the point N is physically significant if it is in the common volume of the two spheres. Hence if we calculate the probability $P_1(w) dw$ to obtain the inequality :

$$w + dw > \frac{|r^q - r^a|}{d_c} > w \quad (37)$$

we find the following expression :

$$P_1(w) = 24 \left(1 - \frac{3}{2} w + \frac{1}{2} w^3 \right) w^2 \quad (w < 1) \\ = 0 \quad (w > 1) \quad (38)$$

Similarly, it is possible to calculate the probability $P_2(w)$ to obtain the inequality :

$$w + dw > \frac{r^q}{d_c} > w \quad (39)$$

and its value is given by :

$$P_2(w) = 24 w^2 \quad (w < \frac{1}{2}) \\ = 0 \quad (w > \frac{1}{2}) \quad (40)$$

The formula (22) can be evaluated by integration by taking into account those probabilities and we obtain :

$$\eta = \frac{12}{5} \left(\frac{\alpha}{4 \pi \epsilon_0} \right)^2 \frac{V_m}{RT \chi_T} \sum_q (R_0^{aq})^{-6} H^{aq} \left[\left(\frac{d_c}{R_0^{aq}} \right)^2 \right] \quad (41)$$

where $H[X]$ is defined by :

$$H[X] = 6 X^{-3} \ln(1 - X) + X^{-2}(1 - X)^{-3} \times \\ \times (6 - 15X + 12X^2 - 3X^3) - 2 \left(1 - \frac{X}{4}\right)^{-3} + 1. \quad (42)$$

If we calculate the finite expansion of $H[X]$, it is given by :

$$H[X] = \frac{21}{20} X^2 + \frac{27}{16} X^3 + \frac{1815}{896} X^4 + 0(X^5). \quad (43)$$

We find again for η the finite expansion (31).

III.3.5 CALCULATION OF THE SIZE OF THE CELLS. —

From the preceding equations, we can deduce the size of the cells in a dense medium from the depolarization of the Rayleigh scattering. We can define a quantity ψ by the following equation :

$$\psi = \frac{1}{2.52 v} \left(\frac{4 \pi \epsilon_0 \sigma^3}{\alpha}\right)^2 \frac{V_m}{RT \chi_T} \left(\frac{\rho_m}{\rho}\right)^2 \eta. \quad (44)$$

Then the formula (31) gives :

$$\psi = \chi^2 + 1.607 \chi^3 + 1.930 \chi^4 \quad (45)$$

where :

$$\chi = \left[\frac{d_c}{\sigma} \left(\frac{\rho}{\rho_m}\right)^{1/3} \right]^2. \quad (46)$$

The crystalline system of Argon is f. c. c. and the value of v is twelve. The theoretical molar volume is equal to :

$$(V_m)_m = N^{\circ} \frac{\sigma^3}{4} \quad (47)$$

N° is the Avogadro's number. The value of ρ_m in Amagat is :

$$\rho_m = \frac{4 (V_m)_0}{N^{\circ} \sigma^3} \quad (48)$$

$(V_m)_0$ is the molar volume in the S. T. P. conditions. If we take the value $\sigma = 3.40 \text{ \AA}$, ρ_m is equal to 1 340 Amagat.

Moreover we see that the measurement of η at high densities [10] and the knowledge of the thermodynamical parameters in (44) allow us to calculate ψ , and hence to obtain χ and d_c . At last, the formula (32) gives D_c . The details of this calculation are given in [13].

III.3.6 NUMERICAL RESULTS FOR ARGON, AND COMPARISON WITH EXPERIMENT. — The use of the cell model is uneasy : the results are different, depending on the definition of the cell. Thus we may compare the dimensions of the cell deduced from depolarization measurements with those deduced from the following considerations : at the density ρ_m , D_c is equal to σ ; at the density ρ , when all the molecules are in the center of their cells we may put a rigid

sphere in the place of a molecule : the diameter D_c of the largest possible sphere is the diameter of the cell and obeys to the following equation :

$$\frac{D_c}{\sigma} = 2 \frac{d}{\sigma} - 1. \quad (49)$$

We draw this curve with dotted line on figure 5. The agreement is satisfying with the value deduced from the depolarization (solid line), but we notice the following difficulty : the geometrical definition of the cell does not allow that two neighbouring molecules have independent displacements, while this hypothesis has been assumed in the preceding calculation. For a better calculation, we must take into account the correlations in the displacements.

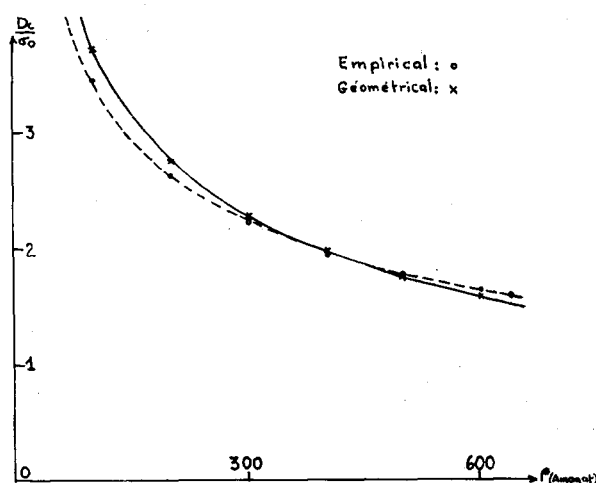


FIG. 5. — Comparison between the experimental and theoretical values of cell diameters versus the density.

However in spite of the crude character of the model, the agreement with experiment is satisfying. It indicates that it's possible to use the study of the depolarization for a thermodynamic knowledge of dense medium.

We see on the figure 6 the values of the experimental and theoretical parameter Y for two other types of

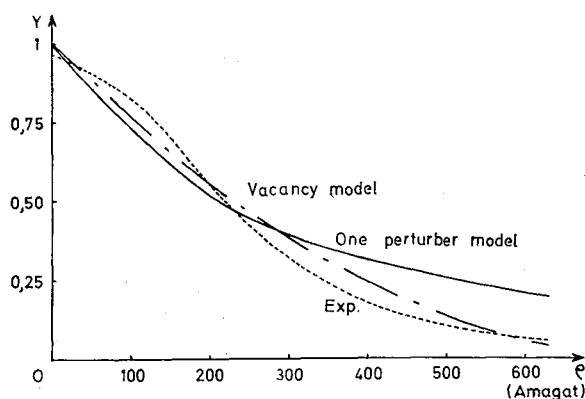


FIG. 6. — Experimental and theoretical values of the interference factor Y versus the density ρ .

model : a vacancy model and a one perturber model. For this last model we make the following assumptions: at mean density, the closed molecules have a random angular distribution but the distant molecules make a regular arrangement which doesn't create some field fluctuations. So we introduce a cut off at a distance R_c . This distance is choiced in order that the number of perturbers for a molecule is one in average. Hence, we can write :

$$n \int_0^{R_c} g(r) d\tau = 1. \quad (50)$$

It's easy to show that η obeys to the following expression :

$$\eta = \frac{12}{5} \frac{V_m}{RT\chi_T} \left(\frac{\alpha}{4\pi\epsilon_0} \right)^2 \int_0^{R_c} \frac{g(r)}{r^6} d\tau. \quad (51)$$

It's clear that we obtain again at low density the formula (8). It's interesting to see that the numerical predicted result for a dense medium is much too high. So, an experimental evidence is given that the interference effects are very strong. The details of calculations are given in [12]. To conclude we'll discuss the validity of the basic assumption and we'll see how the depolarization is connected to other fields of physics.

Conclusions. — DISCUSSION ABOUT THE FUNDAMENTAL HYPOTHESIS. — In this work we connect the fluctuation of the anisotropic part of the dipolar moment to the fluctuation of field. Mazur, Jansen and Mandel [15]-[19] established that it's true, if we neglect the effects of overlapping of the electronics wave functions. We can write for the anisotropic part of the polarizability Δ of a pair the following equation :

$$\Delta = \Delta_{\text{overlapping}} + \Delta_{\text{long range}}.$$

The second term is due to the fluctuation of field, the first term can't be easely calculated, but some calculations have been made with models [22]. With Argon and Methane it seems that the essential contribution is due to the second term, but the study of the optical Kerr effect by Buckingham and Dunmur [1] indicates that it is not always true. An interesting fact has been pointed out by Volterra and co-workers [23]: $\Delta_{\text{overlapping}}$ being a short range effect, is less influenced by the interference effects which play

a great part in the depolarization of the light scattered by a dense medium, and in the spectral profile of the depolarized components. Hence they hope to separate the effects of $\Delta_{\text{overlapping}}$ and of $\Delta_{\text{long range}}$.

By using a short range distribution Bucaro and Litovitz [24] predict correctly the spectral profile at high density. In an opposite side, McTague and co-workers [25], using a value of Δ similar to that predicted by fluctuations of field and approximate calculation of distributions of four molecules, obtain also good results.

CONNECTION WITH OTHER FIELDS OF PHYSICS. — The fluctuations of dipolar moments play an important part in physics for correct calculations of dielectric constant, refractive index, Kerr effect, polarized and depolarized intensities. We can write the variations of polarizability of a colliding pair in the following manner :

	Separated pair	Colliding pair
Isotropic part of (α)	2α	$2\alpha + \alpha_p$
Anisotropic part	0	Δ

— α_p is important for an accurate determination of the dielectric constant and of the refractive index.

— Δ determines the optical Kerr effect and the depolarization.

— Both α_p and Δ determine the wings of the Rayleigh-Brillouin scattered light.

The study of the wings of polarized and depolarized intensities indicates that the mean value of Δ^2 is much more important than the mean value of α_p^2 .

This is in agreement with the predictions of a theory of fluctuations of field [2] and indicates that the analysis of the optical Kerr effect and depolarization are simpler than the one of the dielectric constant. The experimental studies are also easier. The following table, using the results of the calculation of Mazur and co-workers [16]-[19], indicates the effects of the different order of fluctuation.

It can be seen from this work that the study of depolarization is interesting in two fields : optics for the knowledge of elementary mechanisms and thermodynamics for the study of the cooperative effects of perturbations.

Dipolar moment $\underline{\mu}$	=	$\underline{\mu}_{(0)}$	+	$\underline{\mu}_{(1)}$	+	$\underline{\mu}_{(2)}$
Fluctuating term				Field fluctuation of first order		Field and polarizability fluctuation of second order
Physical effect		Brillouin-Rayleigh scattering (BR)		Depolarization η ; wings of BR		Corrected calculations of BR and η
		Dielectric constant and refractive index		Clausius-Mosotti and Lorentz-Lorenz laws		Deviations from the preceding laws
				Induced Kerr effect (I. K. E.)		Corrected I. K. E.

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