

<sup>4</sup>W. W. Wood, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (North-Holland, Amsterdam, 1968), pp. 117–227.

<sup>5</sup>F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**, 939 (1964).

PHYSICAL REVIEW A

VOLUME 7, NUMBER 1

JANUARY 1973

## Depolarization of Light in Atomic Fluids

B. J. Alder\* and J. J. Weis

*Laboratoire de Physique Théorique et Hautes Énergies, 91-Orsay, France*  
and

Herbert L. Strauss<sup>†</sup>

*Department of Chemistry, University of California, Berkeley, California 94720*

(Received 17 March 1972)

The experimental value of the polarizability anisotropy of a fluid is found to be an increasingly smaller fraction of the computer-calculated dipole-induced dipole anisotropy as the density is increased. This leads to the conclusion that the distortion of the polarizability of an individual atom from spherical symmetry produces an anisotropy which opposes and finally dominates the dipolar density anisotropy in determining the intensity of the depolarized light scattering.

During the past few years, a number of measurements of depolarized light scattering have been made on rare gases<sup>1</sup> and other nearly spherical molecules.<sup>2</sup> The reason why the measurements show a light scattering intensity at higher density, which is an order of magnitude less than that expected by extrapolation of the gas-phase results, remains unresolved.<sup>3</sup> In general, the scattering in a system of spherical atoms is due to dipoles produced by a fluctuating anisotropic field. The primary cause of such a field is a temporary asymmetric configuration of the atoms. Such an asymmetric density fluctuation can, however, also distort the electron density distribution of an atom so as to produce a polarizability of that atom which departs from spherical symmetry. In this electron-density-distortion contribution we include all the contributions to the macroscopic polarizability anisotropy due to causes other than the dipole-induced dipole mechanism. At low density, since the field a given atom experiences is that produced by interaction with only one other atom, the light scattering per atom varies linearly with density. At high density, since the neighboring atoms are more spherically distributed, the asymmetry is smaller, and one expects a decrease in the light-scattering intensity. The question of whether asymmetric density fluctuations lead predominantly to just a fluctuating dipole-induced dipole anisotropy or whether they lead predominantly to an anisotropy due to polarizability distortions is important to resolve. The calculation of the density fluctuations is a purely statistical-mechanical problem that can be considered exactly, and comparison with experiment can then establish the relative importance of the polarizability distortion which is dif-

ficult to estimate theoretically.

The statistical-mechanical calculations are difficult to perform rigorously at fluid densities without resort to computers since they involve fourth-order distribution functions. They have been carried out here primarily for hard spheres in the spirit of the van der Waals theory which assigns the attractive forces of real molecules a minor role. However, to check this point, a few systems consisting of atoms with square-well and Lennard-Jones interaction potentials have been studied as well.

The dipolar density fluctuation, which leads to light scattering is characterized by the second-rank tensor

$$T_{ij}^{XY} = \frac{1}{r_{ij}^3} \left( \delta_{XY} - \frac{3X_i Y_j}{r_{ij}^2} \right), \quad (1)$$

where  $X, Y = x, y, z$ . In this formula, the capital-letter indices label the coordinates and the lower-case indices the atoms. The distance between atoms  $i$  and  $j$  is  $r_{ij}$ , and  $\delta$  is the Kronecker  $\delta$ . The light scattering per atom, if there is no electronic distortion, is proportional to the dimensionless quantity

$$S^{XY} = \frac{\sigma^6}{N} \left\langle \left( \sum_{i \neq j}^N T_{ij}^{XY} \right)^2 \right\rangle, \quad (2)$$

that is, the statistical average of the square of the value of one of the tensor elements for a system of  $N$  spheres of diameter  $\sigma$ . This expression is valid in the long-wavelength limit, in which retardation effects are neglected. The tensor  $\bar{T}$  also enters the theoretical expressions for a number of other phenomena such as the dielectric polarization of a nonpolar fluid<sup>4</sup> and the nuclear magnetic relaxation<sup>5</sup>

TABLE I. Calculated values of the dipolar density anisotropy  $S$  at various densities for hard spheres (H. S.) and for molecules interacting with square-well (S. W.) potentials ( $kT/\epsilon = T^* \sim 1$ ) and with Lennard-Jones (L. J.) potentials with  $T^*$  given in parentheses.

$V/V_0^a$	$S^{zz}$	$2S_2^{zz}$	$4S_3^{zz}$	$S_4^{zz}$
1.5—H. S. <sup>b</sup>	0.22	11.46		
1.6—H. S.	0.23	10.25	-18.56	8.52
1.6—H. S. <sup>b</sup>	0.27	10.37		
1.6—S. W. <sup>b</sup>	0.25	9.96		
1.68—L. J. (0.75) <sup>c</sup>	0.21	9.11		
2.0—H. S.	0.43	7.33		
2.0—S. W.	0.32	7.1		
2.83—L. J. (2.52) <sup>c</sup>	0.98	4.95		
3.0—H. S.	0.68	4.23		
5.0—H. S.	0.77	2.27		
10—H. S. <sup>b</sup>	0.62	1.05		
20—H. S. <sup>b</sup>	0.38	0.50		

<sup>a</sup>The reduced volume per atom  $V_0 = \sigma^3/\sqrt{2}$ .

<sup>b</sup>Results for 500 particles; the other calculations are for 108 particles.

<sup>c</sup>The Lennard-Jones calculations used 864 particles,  $\sigma = 3.4 \text{ \AA}$ ,  $\epsilon/k = 120 \text{ }^\circ\text{K}$ .

of helium-3, for example.

The calculation of  $S^{XY}$  by molecular dynamics<sup>6</sup> was broken up into its various components. This was done first of all to check on the accuracy of the results, since for an isotropic system  $S^{XX} = S^{YY} = S^{ZZ}$  and  $S^{XY} = S^{XZ} = S^{YZ}$ . Furthermore, for a traceless tensor<sup>7</sup> we find  $S^{ZZ}/S^{XY} = \frac{4}{3}$ . Finally  $S$  was broken up into its pairwise, triplet, and quadruplet terms, in order to evaluate their relative magnitudes:

$$S = 2S_2 + 4S_3 + S_4,$$

where

$$S_4 = \frac{\sigma^6}{N} \left\langle \sum_{i \neq j, k \neq l} T_{ij} T_{kl} \right\rangle,$$

and where for  $S_3$ ,  $l=j$ , and for  $S_2$ ,  $k=i$  and  $l=j$ .

The results are summarized in Table I. The pairwise term could also be checked by performing the averaging with the known hard-sphere pair-distribution function. In the low-density limit that pairwise term dominates leading to the asymptotic behavior proportional to the density. The pairwise term increases monotonically with density. However, the total value of  $S$  has a maximum value as expected at about the density which corresponds to the critical density of a real fluid. At higher densities,  $S$  decreases due to the large cancellation between the pairwise, triplet, and quadruplet terms. The calculations done for particles interacting with a square-well potential show that the value of  $S$  is rather insensitive to the presence of an attractive part in the intermolecular potential at densities that correspond to the liquid region.

The spectroscopic parameter that can be compared most directly to the calculated results is the value of  $\beta^2/\alpha^2$ , the polarizability anisotropy squared divided by the mean polarizability squared. This quantity is related to  $S^{ZZ}$  (in the absence of polarizability distortion) by

$$\frac{\beta^2}{\alpha^2} = \frac{\alpha^2}{2N} \left\langle \sum_{i,j} [(T_{ij}^{XX} - T_{ij}^{YY})^2 + (T_{ij}^{YY} - T_{ij}^{ZZ})^2 + (T_{ij}^{ZZ} - T_{ij}^{XX})^2] \right\rangle$$

$$= \frac{3\alpha^2}{2N} \left\langle \sum_{X,Y} (\sum_{i,j} T_{ij}^{XY})^2 \right\rangle = \frac{45\alpha^2}{4\sigma^6} S^{ZZ}. \quad (3)$$

The factor  $\frac{45}{4}$  results from the angular averaging<sup>7,8</sup> called for in the definition of  $\beta$ . The first expression for  $\beta^2/\alpha^2$  is to be evaluated in the principal-axis system of a configuration of atoms, the second expression is in a general-axis system attached to the atoms, and  $S^{ZZ}$  is in a space-fixed axis system. The experimental values of  $\beta^2/\alpha^2$  (Table II) are obtained by two methods. In the first the measured depolarization ratio  $\Delta$  can be used directly in the familiar expression

$$\Delta = \frac{\beta^2/\alpha^2}{15kT\rho\beta_T} \quad (4)$$

which relates the polarized and depolarized scattering. In Eq. (4),  $k$  is Boltzmann's constant,  $T$  the absolute temperature,  $\rho$  the number density, and  $\beta_T$  the isothermal compressibility. In using this expression we have justifiably neglected smaller contributions to the isotropic fluctuations.

In the second method, the absolute intensity of the depolarized scattering is used directly to calculate the value of  $\beta^2/\alpha^2$ . This absolute intensity is obtained by comparison to the allowed vibrational bands of gaseous  $\text{CCl}_4$  which in turn have been compared to the theoretically calculated values for the intensities of the rotational lines of the hydro-

TABLE II. Comparison with experiments in liquids.

$\sigma(\text{\AA})$	$V/V_0$	$10^3 \Delta$	$10^3 \beta^2/\alpha^2$ Expt. <sup>a</sup>	$10^3 \beta^2/\alpha^2$ Expt. <sup>b</sup>	$10^3 \beta^2/\alpha^2$ Calc.
Ar	3.4	1.7		0.8 <sup>c</sup>	6.1
Xe <sup>d</sup>	4.1	1.5	$\sim 1$	0.8	8.3
$\text{CCl}_4^e$	5.3 <sup>f</sup>	1.6	19	7.6	15

<sup>a</sup>Deduced from depolarization measurements.

<sup>b</sup>Deduced from intensity measurements in comparison to  $\text{CCl}_4$  bonds.

<sup>c</sup>Reference 1(a). The value of  $\beta^2$  as given in that reference is incorrect [J. P. McTague (private communication)]. It should be  $1.5 \times 10^{-3}$  (without the effective field correction).

<sup>d</sup>Reference 1(e).

<sup>e</sup>Reference 2.

<sup>f</sup>Obtained by taking the melting point as corresponding to  $V/V_0 = 1.5$ .

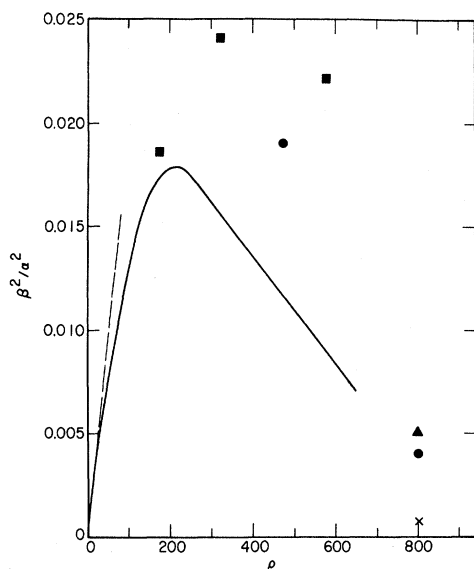


FIG. 1. Polarizability of argon as a function of density in amagats. The solid curve represents the experimental results at room temperature [Ref. 1(c)]. The cross represents the experimental results for liquid argon at 90°K [Ref. 1(a)]. The straight line is the theoretical prediction of the initial slope based on a realistic potential. The squares result from a numerical calculation for hard spheres with a value of  $\sigma$  appropriate to room temperature. The triangle is from the calculation with a value of  $\sigma$  appropriate to 90°K. The circles are from calculations with a Lennard-Jones potential, and the two points are calculated for the two different temperatures.

gen molecule.<sup>9</sup> The results for the value of  $\beta^2/\alpha^2$  for  $\text{CCl}_4$  are listed in Table II and the agreement between the two methods is seen to be excellent. For liquid argon and xenon, the ratio of the scattering intensity is known only with respect to liquid  $\text{CCl}_4$ . This ratio must be corrected by the standard effective field correction  $[\frac{1}{3}(n^2 + 2)]^4$ , where  $n$  is the refractive index,<sup>10</sup> and this corrected ratio is given in Table II. The results for the value of  $\beta^2/\alpha^2$  derived for liquid xenon are in satisfactory agreement with those from Eq. (4) considering the difficulty involved in comparing intensities of the xenon and  $\text{CCl}_4$  measured by different spectrometers.<sup>11</sup>

All the experimental measurements of the intensity must assume that the intensity falls accurately to zero outside the frequency range in which the intensity is large enough to be measured.

Work is now in progress on the autocorrelation function of the dipole anisotropy to theoretically verify this assumption. Finally, it should be pointed out that the liquid-argon and -xenon experiments carried out under nearly corresponding-states conditions lead to values of  $\beta^2/\alpha^2$  of the same magnitude. This is not a necessary result since the value of  $\alpha/\sigma^3$  is not at all the same for these two elements.

The experimental results for argon are compared to the density-anisotropy calculations in Fig. 1. At low densities, it is known that the theoretical slope exceeds the experimental one by about 50% (this is not evident on the graph because of the scale used). The theoretical slope has been recalculated for more realistic pair potentials<sup>12,13</sup> with little change in the result. At higher densities the choice of  $\sigma$  required for comparison to the hard-sphere calculations is based on the values previously derived<sup>14</sup> from the intercept of the high-temperature equation of state which makes  $\sigma$  slightly temperature dependent. Since the results are rather sensitive to the choice of  $\sigma$  (they depend on  $\sigma^6$ ), two additional calculations were carried out using a Lennard-Jones potential. These calculations confirm the results of the hard-sphere calculations. The increasing discrepancy between the calculations and experiment with increasing density is due to the increasingly more effective distortion of the electron distribution and of the polarizability. This distortion arises because the electron density decreases where the local concentration is high and increases where the local concentration is low. In other words, the electron distortion compensates for any density distortion, and at liquid densities, the total polarizability anisotropy is an order of magnitude less than what it would be if the atoms were not deformable. For  $\text{CCl}_4$ , the discrepancy between theory and experiment is a bit smaller, presumably because there is a significant further contribution to the anisotropic polarizability from the distortion of the molecular framework which we have not taken into account.

Most of the computation was carried out under the auspices of the U. S. Atomic Energy Commission at Livermore with the help of Mary Ann Mansigh. We are grateful to her and to Lois Rosenthal for their aid with the calculations. We also are grateful for enlightening discussions with Dr. Thibau.

\*Permanent address: Lawrence Livermore Laboratory, Livermore, Calif.

<sup>1</sup>Supported in part by the National Science Foundation.

<sup>1</sup>(a)P. A. Fleury and J. P. McTague, *Opt. Commun.* **1**, 164 (1969); (b)J. P. McTague, P. A. Fleury, and D. B. DuPré, *Phys. Rev.* **188**, 303 (1969); (c)M. Thibau, B. Oksengorn, and B. Vodar, *J. Phys.* **29**, 287 (1968); (d)M. Thibau, G. C. Tabisz, B.

Oksengorn, and B. Vodar, *J. Quant. Spectrosc. Radiat. Transfer* **10**, 839 (1970); (e) W. S. Gornall, H. E. Howard-Lock, and B. P. Stoicheff, *Phys. Rev. A* **2**, 1288 (1970).

<sup>2</sup>H. S. Gabelnick and H. L. Strauss, *J. Chem. Phys.* **49**, 2334 (1968).

<sup>3</sup>H. B. Levine and G. Birnbaum, *Phys. Rev. Lett.* **20**, 439 (1968); V. Volterra, J. A. Bucaro, and T. A. Litovitz, *Phys. Rev.*

Lett. **26**, 55 (1971), (Ar); J. A. Bucaro and T. A. Litovitz, J. Chem. Phys. **55**, 3585 (1971), (CCl<sub>4</sub>); R. W. Hellwarth, Phys. Rev. **152**, 156 (1966); and Phys. Rev. **163**, 205 (1967) has attempted a calculation similar to ours, but he used the Kirkwood approximation which led to anomalous results at liquid densities. A number of papers consider both mechanisms of light scattering at low densities via an expansion in powers of the density and conclude that the two possible mechanisms oppose each other: W. M. Gelbart, J. Chem. Phys. **57**, 699 (1972); J. P. McTague, W. D. Ellenson, and L. H. Hall, J. Phys. (Paris) **33**, C1-241 (1972); J. P. McTague and G. Birnbaum, Phys. Rev. A **3**, 1376 (1971); H. B. Levine and G. Birnbaum, J. Chem. Phys. **55**, 2914 (1971).

<sup>4</sup>J. G. Kirkwood, J. Chem. Phys. **4**, 592 (1936). This reference points out that terms in higher powers of  $\bar{T}$  are expected to be small.

<sup>5</sup>R. L. Garwin and H. A. Reich, Phys. Rev. **115**, 1478 (1959). These authors conclude that this mechanism plays only a minor

role in the relaxation.

<sup>6</sup>B. J. Alder and T.E. Wainwright, J. Chem. Phys. **31**, 459 (1959).

<sup>7</sup>A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance* (Harper and Row, New York, 1967), Appendix I.

<sup>8</sup>E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

<sup>9</sup>H. W. Schrotter and H. J. Bernstein, J. Mol. Spectrosc. **12**, 1 (1964).

<sup>10</sup>P. D. Maker and R. W. Terhune, Phys. Rev. **137**, A801 (1965).

<sup>11</sup>B. P. Stoicheff (private communication).

<sup>12</sup>J. A. Barker, M. V. Bobetic, and A. Pompe, Mol. Phys. **20**, 347 (1971).

<sup>13</sup>J. H. Dymond and B. J. Alder, J. Chem. Phys. **51**, 309 (1969).

<sup>14</sup>J. H. Dymond and B. J. Alder, J. Chem. Phys. **45**, 2061 (1966).

## Luminescence of Helium II Produced by Weak $\alpha$ -Particle Sources\*

Huey A. Roberts<sup>†</sup> and Frank L. Hereford

*Department of Physics, University of Virginia, Charlottesville, Virginia 22901*

(Received 1 May 1972)

Measurements of the intensity of luminescence produced by weak  $\alpha$ -particle sources in He II are presented for  $0.3 < T < 4.2$  °K, for different chamber sizes, and with an electric field applied in the region of the  $\alpha$ -particle source. With zero field the intensity exhibits a complex behavior, remaining approximately constant between  $T_\lambda$  and 1.2 °K, then dropping to a minimum near 0.6 °K, and rising again at lower temperatures. The application of an electric field (up to 13 000 V/cm) in the source region reduces the intensity above 0.8 °K but increases it at lower temperatures. The transient behavior of the luminescence upon application of a pulsed field is described and discussed. The qualitative features of the temperature dependence of the luminescence are accounted for in terms of radiation from metastable systems, the diffusion coefficient of which rises exponentially ( $\sim e^{\Delta/kT}$ ) as the temperature drops. Approximate values of the diffusion coefficient are presented. The electric-field-induced amplification of the luminescence below 0.8 °K is attributed to metastable interactions with charged vorticity.

### I. INTRODUCTION

The study of the luminescence of superfluid helium produced by charged particles has proved to be a useful means of investigating the microscopic structure of the fluid and, more particularly, of its excitations.

With weak sources of  $\alpha$  particles ( $\approx 10^3$ /sec), the luminescence emitted within approximately  $10^{-6}$  sec following  $\alpha$  emission (scintillation intensity) has been known for some time to be strongly temperature dependent below  $T_\lambda$ .<sup>1</sup> The effect can be accounted for<sup>2</sup> by assuming that collision-induced radiation from some species of metastable states is increasingly delayed as the temperature drops. The diffusion coefficient of the metastables ( $\sim e^{\Delta/kT}$ ) rises, and an increased number escape the vicinity of the  $\alpha$ -particle "track" where a high density of collision partners is initially available. It has not been possible, however, to identify the metastable species involved. With much stronger sources of electrons, the ultraviolet-emission

spectrum has been observed<sup>3</sup> and attributed principally to the radiative dissociation of the  $a^1\Sigma_u^+$  state of the neutral helium molecule.

Unfortunately, it is difficult to correlate these measurements. The inhibition of He II scintillation observed with weak  $\alpha$  sources involves processes associated with single  $\alpha$  particles. With much stronger electron sources ( $\approx 10^{13}$ /sec), the high density of excitation and ionization throughout the source region results in an essentially "steady-state" luminescence which would obscure any effect associated with single-particle phenomena. The effects associated with single  $\alpha$  particles depend also on the fact that the excitation density in the immediate vicinity of each  $\alpha$  "track" is very much greater than the "steady-state" density produced in the spectroscopic studies with electron beams.<sup>3,4</sup>

We report here measurements of the total luminescence produced by weak  $\alpha$  sources, including observation of the effects of varying the chamber dimensions and applying an electric field. The re-