Dielectric constant of atomic fluids with variable polarizability

(pair polarizability/Clausius–Mossotti function)

B. J. ALDER*, J. C. BEERS II†‡, H. L. STRAUSS‡, AND J. J. WEIS†

*Lawrence Livermore Laboratory, P.O. Box 808, Livermore, California 94550; †Department of Chemistry, University of California, Berkeley, California 94720; and ‡Laboratoire de Physique Théorique et Hautes Energies, Université de Paris XI, 91405 Orsay, France, Laboratoire associé au Centre National de la Recherche Scientifique

Contributed by Berni J. Alder, March 10, 1980

ABSTRACT The Clausius–Mossotti function for the dielectric constant is expanded in terms of single atom and pair polarizabilities, leading to contributions that depend on both the trace and the anisotropy of the pair-polarizability tensor. The short-range contribution of the anisotropic part to the pair polarizabilities has previously been obtained empirically from light scattering experiments, whereas the trace contribution is now empirically determined by comparison to dielectric experiments. For helium, the short-range trace part agrees well with electronic structure calculations, whereas for argon qualitative agreement is achieved.

Optical and electrical experiments on fluids indicate that the polarizability of a dense system of noble gas atoms is not simply the sum of the individual atom polarizabilities, regardless of whether these experiments measure the trace or the anisotropy of the polarizability tensor. Examples of properties that depend on the trace are the dielectric constant, the index of refraction, and the isotropic light scattering; the Kerr effect and the depolarized light scattering depend on the anisotropy. All show deviations from the independent polarizability model which can be accounted for most simply by introducing a pair-wise additive pair polarizability.

This pair polarizability can in principle be calculated quantum mechanically as a function of the separation of two atoms, just like the intermolecular potential (1, 2). As for the intermolecular pair potential, the only part of this pair polarizability that is rigorously known (besides the classical part) is the large separation asymptotic term. This term is of the same physical origin as the London dispersion term of the van der Waals attraction and, just like it, decays as A/r^6 , where A is a constant that measures the correlation between the motion of the electrons in a pair of atoms (3, 4). It is a quantum mechanical term, and is labeled QM to distinguish it from the classical dipole-induced dipole (DID) interaction that asymptotically varies with the same power of r . As in the Lennard–Jones potential, we are forced at present to add to the long-range part an empirical term that can be either an exponential or a power law in order to account for the short-range (SR) distortions in the individual polarizabilities due to repulsive interactions between a pair of atoms (5). The constants in this empirical term are deduced by fitting a given type of experiment, and the resulting pair polarizability can then be used to account for other optical and electrical properties. This pair polarizability can also be compared to approximate theoretical predictions.

Unfortunately, the experimental consequences of the deviation from simply additive individual polarizabilities are generally small and therefore difficult to measure accurately. This has been established in a series of calculations (6–9) of different properties in which the quantum mechanical con-

tributions to the pair polarizability were neglected. These contributions were taken into account in calculating the intensity of depolarized light in dense rare gas fluids (10), and the short-range distortions were shown to be required to significantly reduce the intensity in order to agree with the experimental observations. For the dielectric constant, it was shown that the deviations from the Clausius–Mossotti functions are necessarily positive without the introduction of short-range distortions whereas experiments indicate small, but negative, deviations at high density. The purpose of this paper is to establish whether theoretically consistent short-range distortions of the trace can account for these small negative deviations. For these calculations, the short-range distortions of the anisotropic pair polarizability are also required, and these have been taken from the earlier depolarized light scattering analysis (10).

THEORY AND CALCULATION

The Pair Polarizability. The polarizability tensor of a pair of rare gas atoms (11), $\tilde{\alpha}(i, j)$, can be characterized by the isotropic part α and the anisotropy β :

$$\tilde{\alpha}(i, j) = \alpha \tilde{U} + \beta \tilde{D}, \quad [1]$$

in which $\tilde{U}$ is the unit tensor and $\tilde{D}$ is the second-rank irreducible tensor

$$D_{ab}(i, j) = \hat{r}_{ij}^a \hat{r}_{ij}^b - \delta_{ab}/3, \quad [2]$$

in which $\hat{r}_{ij} = \vec{r}_{ij}/|\vec{r}_{ij}|$. Each of these two terms can be broken into a number of contributions. Thus,

$$\alpha = \frac{1}{3} \text{Tr } \tilde{\alpha}(i, j) = 2\alpha_0 + \alpha_{\text{SR}} + \alpha_{\text{QM}} + \alpha_{\text{DID}} \quad [3]$$

and

$$\beta = \alpha_{\parallel} - \alpha_{\perp} = \beta_{\text{SR}} + \beta_{\text{DID}} \quad [4]$$

with

$$\begin{aligned} \alpha_{\text{DID}} &= 4\alpha_0^3/r^6 + 0(\alpha^4/r^9) \\ \alpha_{\text{QM}} &= 5\gamma C_6/9\alpha_0 r^6 \\ \beta_{\text{DID}} &= 6\alpha_0^2/r^3 + 0(\alpha_0^3/r^6). \end{aligned} \quad [5]$$

In these formulas α_0 represents the isolated atom polarizability, so that $\alpha - 2\alpha_0$ measures the deviation from additivity. The symbols $\alpha_{\parallel}$ and $\alpha_{\perp}$ stand for the polarizability parallel and perpendicular to the axis connecting the two particles. The coefficient of the quantum mechanical term, involving the hyperpolarizability γ and the strength of the van der Waals force C_6 , is an approximation to the electron correlation effect (12). The long-range quantum mechanical term in the pair-

The publication costs of this article were defrayed in part by page charge payment. This article must therefore be hereby marked "advertisement" in accordance with 18 U. S. C. §1734 solely to indicate this fact.

Abbreviations: QM, quantum mechanical; DID, dipole-induced dipole; SR, short range.

† Present address: Chevron Research Company, P.O. Box 1627, Richmond, CA 94802.

Table 1. Contributions to the Clausius-Mossotti function for argon

ρ^* ^a	I_6	$\Delta \times 10^3$						Total	Exp. ^c
		$\Delta_{SR}^{(2)b}$	$\Delta_{DID}^{(2)}$	$\Delta_{QM}^{(2)}$	$\Delta_{\beta}^{(3)}$	$\Delta_{\beta DID}^{(3)}$	$\Delta_{\alpha}^{(3)}$		
0.35	1.073	-10.35	7.43	5.76	-2.50	-3.56	— ^d	0.34	0.45
0.50	1.616	-16.59	11.19	8.67	-4.70	-6.96		-1.43	-1.4
0.75	2.742	-32.48	19.00	14.71	-9.20	-15.17	≈ 0.03	-7.97	-8.9
0.90	3.594	-47.57	24.90	19.28	-11.84	-21.53		-15.24	-15.9
1.00	4.248	-61.20	29.43	22.78	-13.38	-26.36	0.06	-22.37	-21.8

^a $\rho^* = \rho\sigma^3$, $T^* = kT/\epsilon = 2.5$; $\sigma = 3.405 \text{ \AA}$; $\alpha_0 = 1.643 \text{ \AA}^3$; $5\gamma C_6/9\alpha_0^2\sigma^6 = 0.00537$.

^b Using Eq. 15.

^c Experimental, from ref. 19.

^d Negligible.

polarizability anisotropy is of higher order than the leading classical term and we neglect it although it is thought to be significant in the interpretation of light scattering data at intermediate densities (11). For the same reason the higher classical terms have been omitted in all calculations. The short-range contributions to the pair polarizability can be represented by either a simple exponential or $1/r^n$ function and will be considered further below.

The Dielectric Constant. The dielectric constant, ϵ , for a system of N nonpolar particles contained in a volume V is given by the Clausius-Mossotti equation (13-15)

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{3V}{4\pi} = \frac{1}{3} \text{Tr} \langle \vec{\alpha}(1, 2, \dots, N) \rangle, \quad [6]$$

in which the polarizability on the right-hand side of Eq. 6 is written as the average value of the N -body polarizability. This

many-body polarizability can be expressed by means of a cluster expansion (14, 15) in terms of irreducible components:

$$\vec{\alpha}(1, \dots, N) = \sum_{i=1}^N \vec{\alpha}^{(1)}(i) + \sum_{i < j} \vec{\alpha}^{(2)}(i, j) + \sum_{i < j < k} \vec{\alpha}^{(3)}(i, j, k) + \dots \quad [7]$$

The one-body polarizability $\vec{\alpha}^{(1)}$, by definition, is just $\alpha_0 \vec{U}$. The difference between the polarizability of a pair and the one-body polarizability is represented by $\vec{\alpha}^{(2)}$ and has been discussed above, whereas the excess triplet polarizability is given by

$$\vec{\alpha}^{(3)}(i, j, k) = \vec{\alpha}(i, j, k) - \vec{\alpha}(i, j) - \vec{\alpha}(i, k) - \vec{\alpha}(j, k) - \vec{\alpha}(i) - \vec{\alpha}(j) - \vec{\alpha}(k). \quad [8]$$

In the large separation limit, the three-body polarizability can

FIG. 1. Trace of the pair polarizability for argon, $\alpha/\alpha_0 \times 10^3$, plotted against the reduced distance, $x = r/\sigma$. The heavily drawn curve is the result of this work; the dashed curve is also the result of this work but with the short-range contribution to the anisotropy omitted; and the light curve is the result of a theoretical calculation (21).

FIG. 2. Trace of the pair polarizability weighted by the pair distribution function, $\alpha(r)g(r)r^2/\alpha_0 \times 10^3$, plotted against the reduced distance, x , for argon and helium at a reduced density of 0.75.

FIG. 3. Parallel, $\alpha_{\parallel}$, and perpendicular, $\alpha_{\perp}$, components of the pair polarizability for argon as a function of the reduced distance, x . The dashed extension of the curve indicates extrapolation to distances where the polarizability is not well determined by experiment.

be rigorously represented by the superposition approximation (14, 15):

$$2\alpha_0\tilde{\alpha}^{(3)}(i,j,k) = \tilde{\alpha}^{(2)}(i,j) \cdot \tilde{\alpha}^{(2)}(j,k) + \tilde{\alpha}^{(2)}(j,i) \cdot \tilde{\alpha}^{(2)}(i,k) + \tilde{\alpha}^{(2)}(i,k) \cdot \tilde{\alpha}^{(2)}(k,j). \quad [9]$$

Use of this approximation at shorter distances in a strongly interacting system, such as that consisting of charged particles (16), is not justified. However, the approximation is likely to be much better for the weakly interacting, noncharged system being considered here. Any small error that might be incurred by its use will be absorbed into the effective pair-wise short-range contribution. With the help of this superposition approximation, which differs in form from the one proposed previously (14, 15), Eq. 6 can be expressed up to triplet terms, by using the definitions introduced in Eq. 1 as,

$$CM = \frac{\epsilon - 1}{\epsilon + 2} \frac{3V}{4\pi N\alpha_0} = 1 + \frac{1}{N\alpha_0} \left\langle \sum_{i < j} \alpha(i,j) \right\rangle + \frac{1}{2N\alpha_0^2} \left\langle \sum_{i < j < k} [3\alpha(i,j)\alpha(j,k) + \beta(i,j)\beta(j,k) \vec{D} \cdot \vec{D}] \right\rangle. \quad [10]$$

FIG. 4. Trace of the pair polarizability for helium, $\alpha/\alpha_0 \times 10^3$, plotted against the reduced distance, x . The heavily drawn curve is the result of this work; the theoretical results are represented by the light curves A (21) and B (22) and the heavy dots (23).

The superposition approximation, as required, is such that when the classical limiting values of α and β are substituted in Eq. 10, the expression reduces to the correct DID limit (17). Introducing the explicit forms for α and β , as given in Eqs. 3–5, leads to

$$CM = 1 + \Delta = 1 + \Delta_{\text{DID}}^{(2)} + \Delta_{\text{QM}}^{(2)} + \Delta_{\text{SR}}^{(2)} + \Delta_{\alpha}^{(3)} + \Delta_{\beta}^{(3)} + \dots,$$

in which

$$\begin{aligned} \Delta_{\text{DID}}^{(2)} &= 2\alpha_0^2 \rho \int g(r)/r^6 d\vec{r} = 4\alpha_0^2 I_6, \\ \Delta_{\text{QM}}^{(2)} &= 5\gamma C_6 I_6 / 9\alpha_0^2 \\ \Delta_{\text{SR}}^{(2)} &= \frac{\rho}{2\alpha_0} \int g(r) \alpha_{\text{SR}} d\vec{r}, \\ \Delta_{\alpha}^{(3)} &= \frac{3}{2\alpha_0^2 N} \left\langle \sum_{i < j < k} \alpha(i,j)\alpha(j,k) \right\rangle, \\ \Delta_{\beta}^{(3)} &= \frac{1}{2\alpha_0^2 N} \left\langle \sum_{a,b} \sum_{i < j < k} \beta(i,j)\beta(j,k) D_{ab}(i,j) D_{ab}(j,k) \right\rangle. \end{aligned} \quad [11]$$

Table 2. Contributions to the Clausius–Mossotti function for helium

ρ^*a	I_6	$\Delta \times 10^3$				$\Delta_{\text{DID}}^{(2)} + \Delta_{\text{DID}}^{(3)}$	$\Delta_{\text{DID}}^{(3)}$	$\Delta_{\alpha}^{(3)}$
		$\Delta_{\text{SR}}^{(2)}$	$\Delta_{\text{QM}}^{(2)}$	Total	Exp. ^b			
0.35	1.438	-8.56	2.53	-6.03	-6.7	0.56		
0.50	2.184	-13.40	3.84	-9.56	-10.1			
0.65	3.018	-19.10	5.31	-13.79	-14.0			
0.75	3.627	-23.43	6.38	-17.05	-17.0			
0.84	4.213	-27.74	7.41	-20.33	-20.2	0.86	-1.70	1
0.95	4.979	-33.55	8.76	-24.8	-24.7			

^a $\rho^* = \rho\sigma^3$, $T^* = kT/\epsilon = 30$; $\sigma = 2.556 \text{ \AA}$; $\alpha_0 = 0.2052 \text{ \AA}^3$; $5\gamma C_6/9\alpha_0^2\sigma^6 = 0.00176$.

^b Experimental, from ref. 19.

and in which ρ is the density, N/V , and $g(r)$ is the pair radial distribution function. Calculations of the pair terms are trivial. Of the triplet terms, only the DID part of $\Delta_{\beta}^{(3)}$ has previously been evaluated in the combination

$$\Delta_{\text{DID}}^{(2)} + \Delta_{\beta\text{DID}}^{(3)} = 5\alpha_0^2 R^{zz}(0)/2\sigma^6 \quad [12]$$

in the notation of the earlier calculation.⁸ Here σ is a characteristic length of the intermolecular potential and

$$R^{zz} = \frac{\sigma^6}{N} \left\langle \sum_{i \neq j, k \neq j} \frac{3}{r_{ij}^3} D_{zz}(i, j) \frac{3}{r_{jk}^3} D_{zz}(j, k) \right\rangle. \quad [13]$$

Although terms up to $\Delta_{\beta}^{(4)}$ have previously been calculated for the interpretation of depolarized light scattering, $\Delta_{\beta}^{(3)}$, which is part of that calculation, could not be extracted. It is calculated here, using β in the form of Eq. 4 with the constants previously determined to force agreement with depolarized light scattering intensities and band shapes (10). Both the Lennard-Jones potential and the sums in the pair and triplet terms have been truncated at 3.2σ . To correct for this truncation, a long-range contribution assuming $g(r) = 1$ has been added to the pair terms and the same correction with opposite sign to the triplet terms. This is justified by consideration of the sums

$$\left\langle \sum_i \left(\sum_{j \neq i} A_{ij} \right)^2 \right\rangle = \left\langle \sum_{i \neq j \neq k} A_{ij} A_{ik} \right\rangle + \left\langle \sum_{i \approx j} A_{ij}^2 \right\rangle.$$

The left-hand side is insensitive to truncation or, equivalently, to the number of particles in the calculation. Therefore, the pair and triplet terms on the right-hand side must have equal and opposite corrections. These corrections have been used to obtain the values given in Tables 1 and 2.

Argon. The procedure for calculating the dielectric constant is to calculate $\Delta_{\text{DID}}^{(2)}$ and $\Delta_{\text{QM}}^{(2)}$ directly from a molecular dynamics calculation by using the Lennard-Jones potential. The three-body term $\Delta_{\beta}^{(3)}$ is calculated in the same way assuming the previously determined β_{SR} for argon (10, 18):

$$\beta_{\text{SR}}/\alpha_0 = -0.118 x^{-9.3}, \quad [14]$$

in which $x = r/\sigma$. The term $\Delta_{\alpha}^{(3)}$ turns out to be negligible. The remaining term, $\Delta_{\text{SR}}^{(2)}$, is determined to account for the difference between all the other terms and experiment (19, 20). This is accomplished by adjusting the constants in the assumed form for α_{SR} . The result is

$$\alpha_{\text{SR}}/\alpha_0 = -0.0196 x^{-12.4}. \quad [15]$$

The magnitude of the various contributions to the Clausius-Mossotti function are listed in Table 1, including the separate value of $\Delta_{\beta\text{DID}}^{(3)}$. The short-range contribution reduces the value of $\Delta_{\beta}^{(3)}$ significantly from the DID value at high densities (by about a factor of 2). A similar effect was observed for the mean-squared anisotropy in the light-scattering intensity calculation (10). By far the largest contribution at high density, however, comes from a decrease in the polarizability of the individual atoms due to the confinement by surrounding particles as expressed by α_{SR} . If β_{SR} is set to zero, $\Delta_{\beta}^{(3)}$ is larger in absolute value and the α_{SR} that is derived is correspondingly smaller:

$$\alpha_{\text{SR}}/\alpha_0 = -0.0148 x^{-9.98}. \quad [16]$$

The exponents in Eqs. 15 and 16 are quite sensitive to the range of experimental data.

The short-range function that has been deduced from dense fluid data (Eq. 15) can also be used to predict the very low density behavior as expressed by the dielectric virial coefficient.

The value thus calculated for the ratio of the second to the first coefficient, $B_2/A_2\sigma^3 = 0.010$ compares well with the experimental value (19) of 0.008 ± 0.001 .

In Fig. 1, the empirically derived values of α/α_0 as a function of the interatomic separation are compared to the results of an electronic structure calculation (21). The values derived from experiment, neglecting the short-range part of the anisotropy, show that the disagreement between the experimentally derived α/α_0 and the calculated ones is not due to the uncertainty in β_{SR} . However, given the approximate nature of the electronic calculation, no more than the qualitative agreement that is observed can be expected.

In Fig. 2, the integrand, $\alpha(r)g(r)r^2/\alpha_0$ is plotted to indicate the separation distances that are most heavily weighted in the analysis of experiments that determine the trace of the polarizability. As shown, this range of reduced distances is between 0.85 and 1.05, a range just short of the first peak in the radial distribution function at $x = 1.1$. Finally, in Fig. 3, we present the perpendicular and parallel components of the pair polarizability as deduced from the empirically determined values $\alpha(r)$ and $\beta(r)$ in order to allow more direct comparison with theoretical calculations. Note that the uncertainties in the empirical curves are amplified in plotting $\alpha_{\perp}$, since this is the difference between the trace and the anisotropy.

Helium. The calculations for helium at room temperature are simpler because, at this high reduced temperature, the higher order terms are smaller, although the total deviation from the Clausius-Mossotti relationship has about the same magnitude as for argon. The smallness of the $\Delta_{\alpha}^{(3)}$ triplet term is demonstrated in Table 2. Furthermore, the sum of the $\Delta_{\text{DID}}^{(2)}$ and $\Delta_{\beta}^{(3)}$ terms is also small because they are of opposite sign and nearly cancel. The error of neglecting these three terms is less than the other approximations in this procedure and the experimental uncertainties. By use of the remaining contributions, $\Delta_{\text{SR}}^{(2)}$ and $\Delta_{\text{QM}}^{(2)}$, α_{SR} was fitted to experiment (19, 20) with the result

$$\alpha_{\text{SR}}/\alpha_0 = -43.1 e^{-8.70x}. \quad [17]$$

A power law form does not fit the data as well. From Table 2 it can be seen that this short-range contribution overwhelmingly determines the deviations from the Clausius-Mossotti equation under the experimental conditions. As seen in Fig. 2, the experiments are most sensitive to the value of $\alpha(r)$ in the range of reduced distances between 0.75 and 1.0, closer in than for argon, as expected. Once again, the calculated ratio of the virial coefficients, $B_2/A_2\sigma^3 = -0.011$ is in good agreement with the experimental value (20) of -0.015 ± 0.002 . Fig. 4 shows that the above determined function $\alpha_{\text{SR}}/\alpha_0$ compares favorably to the theoretically determined pair polarizability (21-23). The better agreement for helium is all the more gratifying, because the theories for the simpler helium atom should be more accurate.

We are pleased to acknowledge illuminating conversations with Prof. W. M. Gelbart. We acknowledge support of the National Science Foundation through a fellowship award to J.C.B. and an award of a research grant to H.L.S.

1. Silberstein, L. (1917) *Phil. Mag.* 33, 92-128.
2. Silberstein, L. (1917) *Phil. Mag.* 33, 521-533.
3. Jansen, L. & Mazur, P. (1955) *Physica* 21, 193-207.
4. Jansen, L. & Mazur, P. (1955) *Physica* 21, 208-218.
5. Michels, A., DeBoer, J. & Bijl, A. (1937) *Physica* 4, 981-994.
6. Alder, B. J., Weis, J. J. & Strauss, H. L. (1973) *Phys. Rev. A* 7, 281-284.
7. Alder, B. J., Strauss, H. L. & Weis, J. J. (1973) *J. Chem. Phys.* 59, 1002-1012.

⁸ In ref. 8, equation 1 should start $R^{zz}(\tau) = \sigma^6/N$ times the sum.

8. Alder, B. J., Strauss, H. L. & Weis, J. J. (1975) *J. Chem. Phys.* **62**, 2328–2334.
9. Alder, B. J., Strauss, H. L., Weis, J. J., Hansen, J. P. & Klein, M. L. (1976) *Physica* **83B**, 249–258.
10. Alder, B. J., Beers, J. C., II, Strauss, H. L. & Weis, J. J. (1979) *J. Chem. Phys.* **70**, 4091–4094.
11. Frommhold, L. (1980) *Adv. Chem. Phys.* **46**, in press.
12. Buckingham, A. D. (1956) *Trans. Faraday Soc.* **52**, 1035–1041.
13. Kaufman, A. N. & Watson, K. M. (1961) *Phys. Fluids* **4**, 931–943.
14. Heller, D. F. & Gelbart, W. M. (1974) *Chem. Phys. Lett.* **27**, 359–363.
15. Gelbart, W. M. (1974) *Adv. Chem. Phys.* **26**, 1–106.
16. Bounds, D. G. & Hinchliffe, A. (1979) *Mol. Phys.* **38**, 717–727.
17. Kirkwood, J. G. (1936) *J. Chem. Phys.* **4**, 592–601.
18. Levine, H. B. & Birnbaum, G. (1971) *J. Chem. Phys.* **55**, 2914–2917.
19. Vidal, D. & Lallemand, M. (1976) *J. Chem. Phys.* **64**, 4293–4302.
20. Vidal, D. & Lallemand, M. (1977) *J. Chem. Phys.* **66**, 4776–4780.
21. Oxtoby, D. W. & Gelbart, W. M. (1975) *Mol. Phys.* **30**, 535–547.
22. Fortune, P. J. & Certain, P. R. (1974) *J. Chem. Phys.* **61**, 2620–2625.
23. Dacre, P. D. (1978) *Mol. Phys.* **36**, 541–551.