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An Equation for Calculating Nitrogen Density from Measurements of Dielectric Constants

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A new equation for determining the density of nonpolar substances based on measurements of dielectric constants is presented. Applying the new equation to nitrogen at a density from 1 to 30 $\text{mol} \cdot \text{L}^{-1}$, the mean deviation of the results calculated from the equation is of the order of 10^{-4}, which is the same as the uncertainty of the experimental data. Owing to its analytical form, the derived equation can be applied to indicate the density of nonpolar substances with a densitometer, without adding error to the experimental uncertainty. This equation is also capable of determining the mean polarizabilities and molecular diameters, which agree well with results from other investigators. We suggest that the equation derived here can be applied to some other nonpolar substances as well.

KEY WORDS: density; dielectric constant; nitrogen.

1. INTRODUCTION

Nitrogen is a nonpolar substance and the relation between its density ρ and its dielectric constant ε is one of the basic properties. The relation can be studied both experimentally and theoretically. Theoretically, there are two approaches. One is to expand the Clausius–Mossotti equation in a power series in density, the coefficients of which are known as dielectric virial coefficients. Major theoretical research has been done in this field [1–4]. The equation for virial coefficients has important theoretical significance, but due to its form in a power series in density, it is difficult

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to use in practice. Alternatively, a simple, accurate formula can be developed for practical purposes. For nitrogen, the liquid is compressible and its density can be changed while the pressure and/or temperature varies. To determine the density, one may measure ε and compare it with the experimental data, a relation between ρ and ε. The ε of nitrogen can be measured in a microwave cavity with a high accuracy [5]. The microwave cavity tuned oscillator (MCTO) is an automatic densitometer [6]. The MCTO measures ε and calculates ρ from the following formula, which is an improved equation on Clausius–Mossotti's relation,

$$\rho=\frac{1}{4\pi N\alpha}\frac{(\varepsilon-1)(2\varepsilon+1)}{3\varepsilon}-\frac{4}{N\pi D^3}\frac{(\varepsilon-1)^2}{3\varepsilon} \tag{1}$$

where N is Avogardro's number, α the mean polarizability, and D the molecular diameter. Equation (1), derived by Boettcher [7], is a useful one. By comparing it with experimental data, Smetana and Norman determined its parameters. Using the equation with determined parameters they successfully measured the density of liquid hydrogen in a microwave cavity [6]. Equation (1) was derived 40 year ago; since then, little practical research has been done. We herein derive an accurate formula for use in measuring instruments.

2. THE MODEL

Both the Clausius–Mossotti and Boettcher's equation exhibit a large departure from experimental values, especially at high densities. To avoid that, it is necessary to derive a new equation. Here we suggest a fluid model for nonpolar substances, such as nitrogen, calculate internal fields in the substances, and then obtain a new equation.

First, we study a nonpolar fluid at high densities. The molecules of the fluid are in a close-packed array with a regular geometric structure [8] similar to that of a crystal. There are two kinds of arrays: cubic face-centered and hexagonal close-packed. The number of nearest neighbors is 12 for each molecule of the two kinds. Any molecule in the fluid is imagined as a vacuum cavity with the diameter of the molecule. When an external electric field is applied, an induced ideal electric dipole occurs in the center of each cavity.

For this model we consider the interaction between the molecule considered and its nearest neighbors and obtain a corrected internal field. Consequently, we obtain

$$\rho=\frac{1}{4\pi N\alpha}\frac{(\varepsilon-1)(2\varepsilon+1)^2}{3\varepsilon[2\varepsilon+1-n(\varepsilon-1)]}-\frac{4(n+m)}{N\pi D^3}\frac{(2\varepsilon+1)(\varepsilon-1)^2}{3\varepsilon[2\varepsilon+1-n(\varepsilon-1)]} \tag{2}$$

where n and m are parameters which should be determined using experimental data, if one wants to use the equation for practical purposes. The derivation procedure is given in the Appendix.

3. RESULTS

To calculate density from Eq. (2), its parameters should be determined from a comparison with experimental data. Using the data for nitrogen from Ref. 9, with a least-squares fit, we determined the values of the parameters in Eq. (2) listed in Table I.

Using Eq. (2) with the parameters determined, the density can be calculated directly by substituting the measured dielectric constant ε into Eq. (2). For nitrogen, the calculated density values and their relative deviations from the data in Ref. 9 are presented in Table II. The values in the second column in Table II are the dielectric constant, ε. The values in the third and fourth columns are the experimental and calculated densities, respectively. The last column is the relative deviation, with its negative or positive sign omitted. For each isothermal datum, the mean squares deviation is given in the last row. The percentage of deviations in the dilute gas region with values higher than 0.001 is 13.6%, and that for the high-density region with values lower than 0.004 is 58.0%. The calculated results in the high-density region are much better than those in the dilute region. The weighted average of the mean squares deviation is 0.0066. Using Eq. (1) to calculate the density of hydrogen, a larger deviation, above the order of 0.001 [10], appears. For nitrogen, using Eq. (1) results in a large deviation, the results are of little interest and are omitted from Table II.

4. DISCUSSION

4.1. Modifying Factor

Comparing Eq. (2) with Eq. (1), we find a modifying factor g

$$g=(2\varepsilon+1)/[2\varepsilon+1-n(\varepsilon-1)] \tag{3}$$

When the fluid changes into a dilute gas, R approaches infinity; from Eq. (A4) in the Appendix $n=0$, and in Eq. (3) $g=1$. Thus, Eq. (2) reduces to Eq. (1). So Eq. (1) is the approximate expression of Eq. (2). In fact, Eq. (1) is a correction to the Clausius–Mossotti relation and Eq. (2) a correction to Eq. (1). When the fluid turns into a dilute gas, both Eq. (1) and Eq. (2) reduce to the Clausius–Mossotti relation. Therefore, in the dilute region the three have the same accuracy. In the high-density region, the modifying

Table I. Parameters in Eq. (2)

T (K)	$1/4N\alpha$ $(\mathrm{mol \cdot L^{-1}})$	$4(n+m)/ND^3$ $(\mathrm{mol \cdot L^{-1}})$	n (mol)	m (mol)
92.00	73.149	−64.573	1.00	0.11933
110.00	74.741	−22.371	0.25	0.05223
143.10	76.105	−17.758	0.05	0.23944
158.20	76.093	−121.687	1.40	0.23446
223.20	76.085	−161.545	1.95	0.20399
273.20	76.107	−160.103	1.95	0.17565
295.80	76.245	−154.655	1.85	0.20125
s[a]	76.015	−17.553	0.00	0.20125

[a] Saturated liquid nitrogen.

Table II. Densities Calculated from Eq. (2) Compared with Values for Nitrogen from Ref. 9

T (K)	ε	ρ (exp.) $(\mathrm{mol \cdot L^{-1}})$	ρ (cal.) $(\mathrm{mol \cdot L^{-1}})$	Deviation $(\times 10^{-4})$
92.0	1.43276	28.912	28.890	7.7
	1.42164	28.156	28.195	14.0
	1.41144	27.532	27.556	8.8
	1.39012	26.224	26.2165	2.8
			mean square deviation = 9.2	
110.0	1.40640	27.311	27.301	3.8
	1.38561	26.006	26.012	2.2
	1.36688	24.831	24.844	5.05
	1.34760	23.642	23.633	3.95
	1.32435	22.170	22.163	3.0
			mean square deviation = 3.7	
143.1	1.34879	23.722	23.7225	2.2
	1.31737	21.757	21.761	1.9
	1.28266	19.555	19.562	4.0
	1.25014	17.465	17.471	3.3
	1.21564	15.213	15.214	0.9
	1.18126	12.925	12.924	0.04
	1.14696	10.592	10.595	3.0

Table II. (*Continued*)

T (K)	ε	ρ (exp.) ($\mathrm{mol \cdot L^{-1}}$)	ρ (cal.) ($\mathrm{mol \cdot L^{-1}}$)	Deviation ($\times 10^{-4}$)
	1.10930	7.978	7.981	4.1
	1.07455	5.505	5.512	12.0
	1.04039	3.020	3.025	15.9
			mean square deviation = 6.7	
158.2	1.31182	21.425	21.4515	1.6
	1.29028	20.054	20.060	2.8
	1.28017	19.409	19.415	3.1
	1.26961	18.732	18.739	3.7
	1.24978	17.456	17.460	2.8
	1.02106	16.888	6.893	3.2
	1.22955	16.136	16.141	3.4
	1.20935	14.812	41.810	1.0
	1.20205	14.326	14.326	0.003
	1.18886	13.445	13.4455	0.35
	1.16946	12.138	12.138	0.25
	1.16301	11.698	11.700	2.1
	1.14861	10.713	10.717	3.5
	1.12791	9.283	9.288	4.9
	1.12468	9.058	9.063	5.4
	1.10758	7.860	7.866	7.1
	1.08727	6.432	6.426	4.9
	1.08613	6.341	6.345	5.9
	1.06673	4.946	4.950	8.2
	1.04895	3.649	3.655	16.0
	1.04618	3.448	3.452	10.0
	1.02827	2.123	2.1375	20.0
			mean square deviation = 7.0	
223.2	1.22604	15.926	15.9315	3.5
	1.19620	13.952	13.9520	0.3
	1.16725	12.000	12.000	0.65
	1.13777	9.977	9.979	2.3
	1.10841	7.929	7.930	0.8
	1.07820	5.777	5.780	4.9
	1.04865	3.631	3.634	8.5
	1.01982	1.495	1.4965	10.0
			mean square deviation = 5.18	

Table II. (*Continued*)

T (K)	ε	ρ (exp.) ($\mathrm{mol \cdot L^{-1}}$)	ρ (cal.) ($\mathrm{mol \cdot L^{-1}}$)	Deviation ($\times 10^{-4}$)
273.2	1.66637	11.953	11.957	3.6
	1.14224	10.294	10.301	6.5
	1.11924	8.695	8.699	5.0
	1.09486	6.975	6.978	4.8
	1.07088	5.254	5.256	4.4
	1.04742	3.544	3.546	5.3
	1.02351	1.772	1.773	8.1
			mean square deviation = 5.5	
298.5	1.16326	11.747	11.745	3.2
	1.13388	9.724	9.728	4.2
	1.10505	7.703	7.705	5.6
	1.07549	5.590	5.596	10.0
	1.04697	3.510	3.518	20.0
	1.01816	1.371	1.375	28.0
			mean square deviation = 15.0	
Saturation				
63.15[a]	1.46803	30.998	30.923	24.0
65.00	1.46509	30.757	30.749	2.6
70.00	1.45228	29.982	29.987	1.6
75.00	1.43905	29.185	29.196	3.9
80.00	1.42543	28.362	28.379	5.9
86.00	1.40830	27.325	27.345	6.9
92.00	1.39013	26.224	26.241	6.4
98.00	1.37055	25.028	25.043	5.9
102.00	1.35642	24.161	24.172	4.6
106.00	1.34188	23.217	23.229	4.6
110.00	1.32436	22.170	22.179	3.9
114.00	1.30528	20.973	20.979	2.8
116.00	1.29452	20.293	20.299	2.9
118.00	1.28261	19.535	19.540	2.8
120.00	1.26895	18.664	18.666	0.23
122.00	1.25267	17.615	17.617	1.2
124.00	1.231055	16.212	16.211	1.85
125.00	1.215465	15.190	15.187	1.8
126.20[b]	1.55595	11.200	11.198	1.5
			mean square deviation = 4.5	

[a] Triple point.

[b] Critical point.

factor g becomes greater than 1 and the results calculated from Eq. (2) are more accurate than those calculated from Eq. (1) and the Clausius–Mossotti relation.

4.2. Mean Polarizabilities and Diameters of Molecules

There are two important physical quantities included in the parameters in Eq. (2): the polarizability, α, and the diameter of the molecule, D. The former can be determined from Eq. (2) as the density approaches zero. But the latter in the term $[4(n+m)/N\pi D^3]$ cannot be determined directly. To find D, taking a series of values of n, we substitute this expression into Eq. (2) and fit its two parameters. The values for the first dielectric virial coefficient A calculated with the data in the fourth column in Table II are given in the second column in Table III. The mean polarizabilities, α, are obtained from the relation, $\alpha = 3A/4\pi N$, and are listed in the third column in Table III. The diameters D of the molecule, obtained from Eq. (2), are given in the fourth column. For comparison, D values from Eq. (1) are listed in the last column. Values of α and D conform with the results of other investigators [8, 9, 11, 12], as listed in the last few rows in Table III. A and α are 0.14% less than the results of other investigators. In the model, the molecular diameter is defined as the nearest distance between nearest neighbors. In this sense, the results listed in Table III coincide with those in the literature [8, 12]. Furthermore, in Table III we list the

Table III. A Comparison of Polarizabilities and Diameters of Molecules with the Results from Refs. 8, 9, 11, and 12

T (K)	A ($\mathrm{cm^3 \cdot mol^{-1}}$)	α (Å^3)	D (Å^3)	
92.00			3.06	—
110.00			3.055	8.42
143.10	4.3864	1.7389	3.054	5.03
158.20	4.3804	1.7365	3.050	5.08
223.20	4.3883	1.7396	3.044	5.30
273.20	4.3815	1.7369	3.039	5.50
298.50	4.3742	1.7340	3.038	5.86
Others	4.3889 [9]	1.7399 [9]	3.0 [12][a]	
		1.7397 [11]	3.13 [8][b]	
			3.15 [12][a]	

[a] The van der Waals diameter.

[b] The molecular diameter at critical temperature.

molecular diameters calculated from Eq. (2) depending on the temperature. This obeys the law

$$D = D_o(1 + C/T)^{1/2} \tag{4}$$

where D_o is the diameter of the molecule when the temperature approaches infinity. C is a system-dependent parameter. D_o and C are determined by least-squares fits, and their values are $D_o = 3.0266$ Å and $C = 2.2749$ K, respectively.

It goes without saying that as the temperature increases, the diameter decreases. But Boettcher's Eq. (1) is not able to explain this. Another problem with Eq. (1) is that at a temperature between 110 and 92 K, the molecular diameter would become infinite and then negative. This is a discrepancy with the law of Eq. (4). Thus, we have to apply a negative sign to the $T = 92$ K isotherm in the last column in Table III.

4.3. Application

One can calculate the density of nitrogen with the aid of Eq. (2) with a deviation as small as 6.6×10^{-4}, which is the same as the uncertainty of the experimental data. Thus, the calculated results have the same accuracy as the experimental data. To measure ε with the MCTO, one does not need to search for the density values in a book of experimental data, but can obtain the values directly from a computer connected to the MCTO without introducing error in addition to that of the measurement through calculating Eq. (2).

The purpose of this research is to establish an accurate relation between dielectric constant and density. The density values of nitrogen, reported in 1974, are adopted here as an example of the practical application of Eq. (2). Furthermore, we may expect that the equation also will be suitable for some other nonpolar substances.

APPENDIX

Suppose that an external field $\mathbf{E}$ is applied to a spherical cavity in a continuous medium with dielectric constant ε. Considering its boundary conditions, a solution, given in Ref. 7, of Laplace's equation is expressed as two fields, inside and outside the cavity:

$$\mathbf{E}_{\text{in}} = 3\varepsilon\mathbf{E}/(2\varepsilon + 1) \tag{A1}$$

and

$$\mathbf{E}_{\text{out}} = E + 2(D/2R)^3\,(1-\varepsilon)\,\mathbf{E}/(2\varepsilon+1) \tag{A2}$$

where D is the "molecular diameter," and R is a length parameter, the distance from the center of the cavity. Suppose that $\mathbf{E}_{\text{out}}$ applies only to nearest neighbors, and not to those besides the nearest. The $\mathbf{E}_{\text{out}}$ of a nearest neighbor, like a new field, acts upon the molecule considered. In our model there are 12 nearest molecules around the one under consideration. So the second term in Eq. (A2) should be multiplied by 12, i.e., $24(D/2R)^3\,(1-\varepsilon)\,\mathbf{E}/(2\varepsilon+1)$, and applies to the molecule considered. For this reason, Eq. (A1) becomes

$$\mathbf{E}_{\text{in}} = [3\varepsilon/(2\varepsilon+1)][1 + n(1-\varepsilon)/(2\varepsilon-1)]\,\mathbf{E} \tag{A3}$$

where n is a parameter of the reduced distance, in the form of

$$n = 24(D/2R)^3 \tag{A4}$$

When an external field is applied, the molecule considered is taken as a cavity with an ideal point dipole in the center. The field produced by the dipole, like an external field, can polarize the medium around it. The polarized medium, of course, produces a corresponding field. The field produced, called a reaction field, reacts on the dipole. The nearest neighbors do the same. Their reaction fields act not only on the corresponding dipoles, but also on the nearest-neighbor dipoles, including the dipole of the molecule considered. For nonpolar molecules, the ideal dipole moment $\boldsymbol{\mu}$ is determined by the internal field $\mathbf{E}_{\text{i}}$, $\boldsymbol{\mu} = \alpha\mathbf{E}_{\text{i}}$, where α is the mean polarizability. Similarly, for a dipole field a solution of Laplace's equation may also be expressed as the inside or outside field. The inside field of a cavity is given in Ref. 7.

$$\mathbf{E}_{\text{r in}} = m(2\varepsilon-2)\,\mathbf{E}_{\text{i}}/(2\varepsilon+1) \tag{A5}$$

where

$$m = \alpha/(R - D/2)^3 \tag{A6}$$

The outside reaction field is

$$\mathbf{E}_{\text{r out}} = -12 \times 2(a/R^3)(2\varepsilon-2)\,\mathbf{E}_{\text{i}}/(2\varepsilon-2) \tag{A7}$$

where 12 represents the number of nearest neighbors. As discussed above, the reaction field $\mathbf{E}_i$ can be expressed through a combination of Eqs. (A5) and (A7):

$$\mathbf{E}_r = \mathbf{E}_{r\,in} + \mathbf{E}_{r\,out} = [(n+m)/(D/2)^3](2\varepsilon - 2)\,\mathbf{E}_i/(2\varepsilon + 1) \tag{A8}$$

The term in the brackets in Eq. (A8) is a correction to the interaction between the molecule considered and its nearest neighbors. The total internal field $\mathbf{E}_i$ acting on the considered molecules is

$$\begin{aligned}\mathbf{E}_i &= \mathbf{E}_{in} + \mathbf{E}_r \\ &= [3\varepsilon/(2\varepsilon+1)][1 + n(1-\varepsilon)/(2\varepsilon+1)] \\ &\quad \times \mathbf{E}/[1 - (n+m)(2\varepsilon - 2)/(D/2)^3\,(2\varepsilon+1)]\end{aligned} \tag{A9}$$

It is well-known that the strength of polarization **P** varies with α, ρ, and $\mathbf{E}_i$, i.e.,

$$\mathbf{P} = \alpha N \rho \mathbf{E}_i \tag{A10}$$

In addition, **P** is proportional to the applied field **E**, that is,

$$\mathbf{P} = [(\varepsilon - 1)/4\pi]\,\mathbf{E} \tag{A11}$$

Substitution of Eqs. (A11) and (A10) for Eq. (A9) yields Eq. (2).

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