A PARAMETRIC METHODOLOGY FOR THE ASSIGMENT OF PRESSURE VALUES VERSUS REFRACTIVE MEASUREMENT

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Abstract:

The 18SIB04 QuantumPascal EMPIR project aims to achieve quantum-based pressure standards. One of the most promising ways of achieving this goal is the use of a Fabry-Perot interferometer for measuring the refractivity of the involved gas.

The refractivity and gas pressure are connected by the Claussius-Mossotti and Lorenz-Lorentz formal relations. However, these relations are based on "ideal assumptions". The main scope of this research is how to solve this problem minimizing the use of the refractivity virial expansion by a parameter modifying the Lorenz-Lorentz relation. This methodology increases the physical quantum knowledge of the involved gases and develops a new procedure for determining the gas pressure from refractivity measurements.

Keywords: Gas pressure; virial coefficients; Lorenz-Lorentz eq.; refractivity

1. INTRODUCTION

The Lorenz-Lorentz relation showed in equation (1), is written in terms of the refractive index (n), the polarizability (α), the number of particles - atoms or molecules- (N) and the vacuum permittivity (ϵ_0). It mathematically establishes a relation between the polarizability and the refraction index under ideal conditions: "*the assumption that the atoms or molecules are small conducting spheres whose mutual distances are large compared to their diameters*"

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N\,\alpha}{3\,\epsilon_0}. \tag{1}$$

The solution considered above was to use the virial expansion of equation (1) obtaining the equation (2), where $A_R = \frac{4\,\pi}{3}\alpha$ and it depends on the wavelength, B_R and C_R depend on temperature and the wavelength [5]. It is shown a similarity with the thermodynamic virial expression.

$$\frac{n^2 - 1}{n^2 + 2} = A_R\rho + B_R(T)\rho^2 + C_R(T)\rho^3 + \cdots. \tag{2}$$

However, this expansion does not provide information on stereo volume shape and molecular interactions, linked to the quantum characteristics of the problem.

For this research, we have considered more realistic conditions:

1. The atoms or molecules are not considered as small conducting spheres.
2. Steric Form that could induce a tensorial polarizability consideration.
3. Equation (1) is substituted by equation (3), where η is a parameter that refers to the spatial shape of the atoms or molecules and also to cooperative effect due to compressibility related with the stereo compatibility of atoms or molecules

$$\frac{n^2 - 1}{n^2 + \eta} = \frac{N\,\alpha}{3\,\epsilon_0}. \tag{3}$$

2. DESCRIPTION OF THE WORK

Firstly, a bibliographic research of the pressure and refractivity virial coefficients for different gas types was made for different wavelengths and temperatures. Then, the value of the virial coefficients and molar polarizability at a wavelength of 633 nm of Helium, Neon, Argon, Nitrogen, Carbon dioxide, Methane and Hydrogen dioxide are using. This wavelength was chosen due to it is the one in our experimental set-up.

2.1. η parametric estimator

The parameter η was estimated using equations (1) and (2), for a temperature of 323 K except for Neon that a temperature of 273 K was used. This selection of temperatures is due to the amount of data available, as most of the coefficients were given to these temperatures.

In Figure 1 the absolute deviation of the η parameter from 2 is shown, in order to analyse the

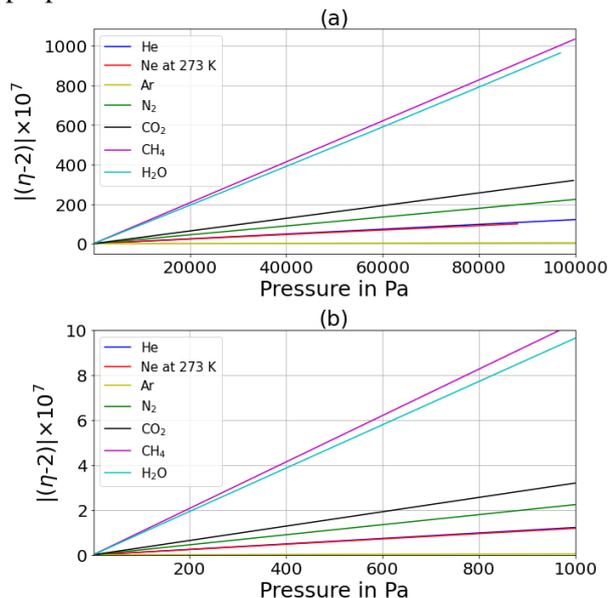change between the ideal assumption and the model proposed in this work.

Figure 1: Absolute value of the deviation of η from 2 depending on the pressure, in a range from 0 Pa to 10 000 Pa for (a) and from 0 Pa to 1 000 Pa for (b), for several gas types at a temperature of 323 K, except for Neon, which was calculated for 273 K.

As it is shown in Figure 1 the value η has a linear evolution with pressure. The slope of the curve for each gas type is calculated and presented with its uncertainty (calculated with the covariance matrix obtained from the non-linear least squares fit) in Table 1.

Table 1: Values of slope of η and its uncertainty for different gas types at a temperature of 323 K, except for Neon that was calculated for 273 K.

Gas	Slope of $\eta \times 10^{10}$ (Pa^{-1})	u (Slope of η) $\times 10^{15}$ (Pa^{-1})
He [11], [10], [14]	-1.21691459	0. 042
Ne at 273 K [7], [10], [12]	-1.134716	3.6
Ar [1], [3], [10]	0.044495968	0.0035
N_2 [1], [6], [7]	2.23558402	0.032
CO_2 [1], [2], [7]	3.208350	1.1
CH_4 [1], [3]	10.349728	1.8
H_2O [4], [9], [13]	9.95208	26

The gas with the smallest slope analysed is the Argon, so it can be called the most ideal gas of the list. Helium and Neon show negative slopes, this may be due to the shape symmetries.

2.2. Residual virial coefficient

If now the virial expansion formula is used with equation (3), it is possible to obtain a virial coefficient called the "*residual virial coefficient*". This parameter shows how well this model fits to a more realistic estimation of the phenomena. In Figure 2 the refractivity virial coefficient is shown

for η = 2 and η ≠ 2. A difference of several orders of magnitude is shown for every molecule. The molecule with less reduction is the Argon.
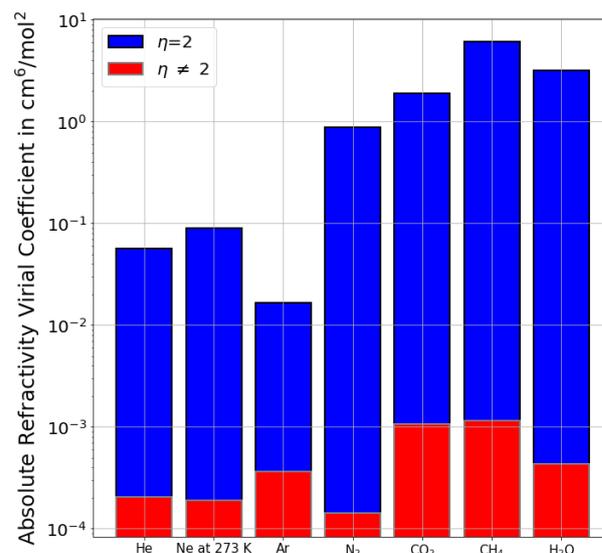

Figure 2: Comparison of the second refractivity virial coefficient when $\eta = 2$ and $\eta \neq 2$.

The Figure 2 shows that our model is consistent as it reduces the virial coefficient without changing the polarizability.

2.3. Shape Factor

The Lorenz-Lorentz relation is obtained under the assumption of spherical symmetry. This assumption has effect in the calculation of divergence of the scalar potential. If a generic geometry is supposed, the Lorenz-Lorentz equation transforms from equation (1) to equation (4), where r is the shape factor

$$\frac{n^2 - 1}{3(n^2 \epsilon_0 r - \epsilon_0 r + 1)} = \frac{N \alpha}{3 \epsilon_0} = A_R \rho . \quad (4)$$

If only the shape factor is taken into account, it can be related to η using equation (5), obtained by combining equations (3) and (4)

$$r = \frac{1}{3 \epsilon_0} \left(\frac{n^2 + \eta - 3}{n^2 - 1} \right). \quad (5)$$

Table 2 is obtained calculating the values of the shape factor for the gas types analysed in Figure 1, where the uncertainty was calculated with the covariance matrix obtained from the non-linear least squares fit. It is shown that the shape factor for Helium and the Neon is lower than the ideal molecule, this can be correlated to the negative value of the slope of η. Also, for Argon the value is almost the same, as it happened with the η parameter.

Table 2: Values of the shape factor and its uncertainty – u- for different gas types at a temperature of 323 K, except for Neon that was calculated for 273 K. Also, the value for an ideal molecule is added ($1/(3\,\varepsilon_0)$) in S.I. and $4\,\pi/3$ in C.G.S.).

Gas	Shape Factor (F/m) $\times 10^{-10}$	u (Shape Factor) in F/m $\times 10^{-16}$
He	2.976045	16
Ne at 273 K	3.428299	15
Ar	3.76826805	0.23
N_2	3.93417082	0.14
CO_2	3.92673783	0.08
CH_4	4.29400680	0.09
H_2O	4.64084458	0.32
Ideal Molecule	3.76469689	--

It was shown that the value of the shape factor does not depend on pressure up to 100 kPa. Nevertheless, a temperature difference was observed as it is shown in Figure 3. Where the values of the refractivity virial coefficients depending on the temperature were used.
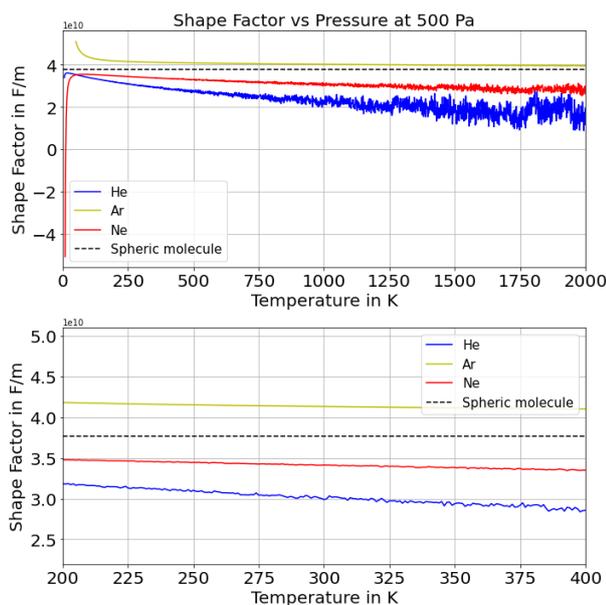

Figure 3: Temperature difference of the Shape Factor for (a) a range from 0 K to 2000 K and (b) a range from 250 K to 350 K. Data obtained from [8].

Figure 3b shows that this methodology presents a small linear dependence in a temperature range of 100 K. This small linear dependence has an inherent progressive ordination value, while the equivalent dependence in the virial coefficients have stronger non-linear dependence and in non-natural order. These results show an improvement from the use of virial coefficients as the use of this factor deletes the virial coefficient.

3. SUMMARY

The ideal assumption of the Claussius-Mossotti and Lorenz-Lorentz relations was solved with the virial expansion coefficients. However, these relations can be solved for real molecules - "no ideal molecules"- using a shape parameter η. The use of this parameter may be established to develop a new methodology for measuring gas pressure via the refractivity whose validity based on the minimization of the virial coefficient expansion. This minimization was already shown with lower value in the *residual virial coefficient* results.

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