Temperature Dependence of the Second Dielectric Virial Coefficients of Rare Gases

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Second dielectric virial coefficients $B_\varepsilon(T)$ of the rare gases Ne, Ar, Kr, and Xe are calculated in a broad range of temperature using accurate HFD-type interatomic interaction potentials and available information on the trace of the pair polarizability $\Delta\alpha$. It is shown that the experimentally determined temperature-variation of $B_\varepsilon(T)$ cannot be reproduced by existing theories. However, it is observed that the reduced dimensionless form of $B_\varepsilon(T)$ follows a remarkably regular pattern, strongly resembling the sign-inverted temperature variation of the second density virial coefficient $B_\varrho(T)$ with the same Boyle-temperature.

1. Introduction

Studies of the dielectric properties of imperfect gases and of their density and temperature variations yield information on interactions between colliding molecules. The Clausius-Mossotti function of a dense gas can be written in the form of a virial equation of state by expanding it in powers of molar density ϱ:

$$\frac{\varepsilon-1}{\varepsilon+2}\varrho^{-1}=A_\varepsilon(T)+B_\varepsilon(T)\varrho+C_\varepsilon(T)\varrho^2+\cdots, \qquad (1)$$

where T is the temperature, ε is the relative permittivity, and the expansion coefficients $A_\varepsilon(T)$, $B_\varepsilon(T)$, ... are called first, second, etc., dielectric virial coefficients. The coefficients $A_\mathrm{R}(\omega,T)$, $B_\mathrm{R}(\omega,T)$, ... of a similar expansion of the molar refraction (the Lorentz-Lorenz function with $\varepsilon=n^2$ in (1), n being the refractive index and ω is the frequency of the applied electromagnetic field) are known as first, second, etc., refractivity virial coefficients.

Dielectric or refractivity virial coefficients are obtained by measuring the relative permittivity ε or the refractive index n as a function of the real gas pressure P, not of its density ϱ, which is difficult to determine independently. Equation (1) can be recast by combining it with the ordinary thermodynamic virial equation of state

$$\frac{P}{RT}\varrho^{-1}=1+B_\varrho(T)\varrho+C_\varrho(T)\varrho^2+\ldots \qquad (2)$$

to become

$$\frac{\varepsilon-1}{\varepsilon+2}=A_\varepsilon\left(\frac{P}{RT}\right)+(B_\varepsilon-A_\varepsilon B_\varrho)\left(\frac{P}{RT}\right)^2+\ldots, \qquad (3)$$

where $B_\varrho=B_\varrho(T)$ is the second and $C_\varrho(T)$ the third density virial coefficient. It was early recognized [1] that a small experimental error in the $A_\varepsilon B_\varrho$ product leads to a large error in B_ε because of its small relative value, e.g., for rare gases at room temperature, B_ε is by two orders of magnitude smaller than the $A_\varepsilon B_\varrho$ product, where B_ϱ is typically known with an uncertainty of a few percent. To overcome this difficulty, a differential expansion technique developed by Buckingham et al. [2] is commonly employed for absolute measurements of the dielectric or refractivity virial coefficients, which allows to eliminate B_ϱ from the final expressions used to determine B_ε and C_ε. This procedure was described in detail in [3–5]. Despite a considerable progress made during the last decade in improving the accuracy of the measurements of the second (and higher) dielectric and refractivity virial coefficients for atomic and several simple molecular gases, absolute measurements of B_ε and B_R are still few in number and difficult to implement. Systematic errors may remain a problem, because the data reported by different groups, or even the same group, sometimes deviate far beyond the stated error margins [4–8].

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The first dielectric virial coefficient, which we assume to be temperature-independent here [9], is proportional to the volume dipole polarizability α_0 of an isolated atom:

$$A_\varepsilon = \frac{4\pi N_{\mathrm{A}}}{3}\alpha_0, \tag{4}$$

where N_{A} is Avogadro's number.

The second dielectric virial coefficient describes the effect due to binary collisions and depends on the averaged collision-induced increment of the trace polarizability

$$\Delta\alpha(R) = \tfrac{1}{3}\,\mathrm{Tr}\,\hat{\alpha}_{12}(R) - 2\alpha_0 = 2(\bar{\alpha}_{12}(R) - \alpha_0), \tag{5}$$

where R is the interatomic separation and $\hat{\alpha}_{12}(R)$ is the polarizability tensor of the colliding pair. For a gas of species interacting via a central potential $V(R)$, the classical statistical mechanics yields [10]

$$\begin{aligned} B_\varepsilon(T) &= \frac{8\pi^2 N_{\mathrm{A}}^2}{3}\int_0^\infty \Delta\alpha(R)\exp[-V(R)/kT]\,R^2\,\mathrm{d}R \\ &= A_\varepsilon 4\pi N_{\mathrm{A}}\int_0^\infty \left[\frac{\bar{\alpha}_{12}(R)}{\alpha_0} - 1\right] \\ &\quad\cdot \exp[-V(R)/kT]\,R^2\,\mathrm{d}R. \end{aligned} \tag{6}$$

Equation (6) is the basic statistical relationship which allows to predict the $B_\varepsilon = B_\varepsilon(T)$ dependence in terms of the temperature dependence of the binary distribution function.

In what follows, we make no distinction between the second dielectric and refractivity virial coefficients, although in the latter case (6) becomes, strictly speaking, less rigorous [11]. However, the differences between B_ε and B_{R} measured at $\lambda = 633$ nm are for the atomic gases within the scatter of the reported experimental values [8].

The purpose of this paper is to calculate in a broad range the temperature variation of the second dielectric virial coefficients for Ne, Ar, Kr, and Xe using the available information on the $\Delta\alpha(R)$ functions (5) and accurate Hartree-Fock-damped-Dispersion interatomic interaction potential functions $V(R)$ in (6). We compare the computed results with the available experimental data on $B_\varepsilon(T)$ and $B_{\mathrm{R}}(T)$, as well as with the results of previous calculations [12] based on a conventional Lennard-Jones (12:6) potential. It is found that invoking more accurate potentials does not improve overall agreement with the experiment, which remains quite poor.

We show that the experimental second dielectric and refractivity virial coefficients plotted in a reduced dimensionless form follow a remarkably regular pattern, strongly resembling the sign-inverted temperature variation of the reduced classical thermodynamic virial coefficient with the same Boyle temperature, and discuss possible implications concerning the collision-induced trace.

2. Input Parameters

The Collision-Induced Polarizability

As was suggested, e.g., in [13] and [14], the collision-induced trace can be approximated by a sum of the leading dipole-induced dipole (DID) and dispersion contributions (disp), and of the short-range contribution (sr):

$$\begin{aligned} \Delta\alpha(R) &= \Delta\alpha_{\mathrm{did}}(R) + \Delta\alpha_{\mathrm{disp}}(R) + \Delta\alpha_{\mathrm{sr}}(R) \\ &= 4\alpha_0^3 R^{-6} + \left(\frac{5\gamma C_6}{9\alpha_0}\right) R^{-6} - \lambda_t \exp(-R/R_t), \end{aligned} \tag{7}$$

where γ is the second hyperpolarizability, and C_6 is the dispersion force constant. The first two long-range terms in (7), both positive (we take $C_6 > 0$ here), are of comparable importance. The negative term, where λ_t and R_t are fitting parameters, models the short-range contribution due to electronic overlap and exchange effects.

Systematic calculations of the static collision-induced pair polarizabilities for the Ne, Ar, Kr, and Xe diatoms have been reported by Dacre [15–17]. Full *ab initio* calculations including configuration interaction (CI) that should, in principle, account for all contributions in (7), have been carried out only for neon [15]. For heavier rare gases, the results were obtained at the SCF level [16, 17], which neglects the CI effects and thus does not take into account the dispersion contribution. In order to compensate for the deficiencies of the SCF approximation, it was proposed [17, 18] to rescale $\Delta\alpha_{\mathrm{scf}}(R)$ and to write the collision-induced trace as

$$\Delta\alpha(R) = \Delta\alpha_{\mathrm{disp}}(R) + \Delta\alpha_{\mathrm{scf}}(R) \times (\alpha_0^{\mathrm{exp}}/\alpha_0^{\mathrm{scf}})^3, \tag{8}$$

where $\Delta\alpha_{\mathrm{disp}}(R)$ is the dispersion term explicitly given in (7), α_0^{exp} the experimental static polarizability, α_0^{scf} the SCF polarizability, and the exponent in the scaling factor is the same as in the lowest-order DID term. The electrooptic parameters of isolated atoms used in the present calculations are collected in Table 1.

Table 1. Electric and potential parameters of rare gas atoms.

	Ne	Ar	Kr	Xe
ε/k, K [a]	42.25	143.25	201.3	282.8
R_m, a.u. [a]	5.8411	7.1073	7.5797	8.2498
σ, a.u. [a]	5.214	6.342	6.748	7.353
$A \cdot 10^{-4}$ [a]	89.572	11.321	6.974	5.441
a [a]	13.8643	9.0005	8.3880	7.5296
b [a]	0.1299	2.6027	2.7961	3.3390
D [a]	1.36	1.04	1.208	1.114
C_6, a.u. [b]	6.383	64.30	129.6	285.9
$C_8 \cdot 10^{-2}$, a.u. [a]	0.965	16.1	39.48	112.14
$C_{10} \cdot 10^{-4}$, a.u. [a]	0.152	5.86	17.0	61.96
α_0^{exp}, a.u. [c]	2.669	11.08	16.79	27.16
α_0^{scf}, a.u. [d]	2.697 [e]	10.384	16.069	25.59
γ, a.u. [f]	108.0	1167	2600	6888

[a] Refs. [19–21], [b] Ref. [22], [c] Ref. [12], [d] Refs. [15–17], [e] SCF +CI polarizability, Ref. [15], [f] Refs. [23, 24].

The Potential

A number of realistic Hartree-Fock-damped-Dispersion (HFD) interatomic potentials for the ground-state rare gas atoms have been developed in recent years by Aziz et al. [19–21]. In reduced form, $V(R) = \varepsilon V^*(x)$ with $x = R/R_m$, where ε is the well depth and R_m is the position of the minimum, the HFD potential is

$$V^*(x) = A \exp(-ax - bx^2) - F(x) \sum_{j=0}^{2} C_{2j+6}/x^{2j+6}, \tag{9}$$

where

$$\begin{aligned} F(x) &= \exp[-(Dx^{-1} - 1)^2], \quad x < D, \\ F(x) &= 1, \quad x \geq D \end{aligned} \tag{10}$$

is the damping function, which suppresses the divergence of the long-range part at small interatomic separations (damping constant D in Table 1).

These multiparametric HFD potentials were demonstrated [19–21] to accurately reproduce a broad variety of the macroscopic properties (second density virial coefficients, viscosity and other transport data, heats of sublimation) and microscopic properties (spectroscopic parameters of van der Waals dimers, scattering cross sections) of rare gases and can be regarded as exact in the context of the present work. Parameters of the HFD potentials are listed in Table 1. For comparison, we also present below the results obtained using (12:6) potentials with the force constants derived from viscosity [12].

3. Results and Discussion

We computed the second dielectric virial coefficients $B_\varepsilon(T)$ for the gases Ne, Ar, Kr, and Xe using the HFD potentials and the *ab initio* data on $\Delta\alpha_{\mathrm{scf}}(R)$ tabulated by Dacre [15–17]. The expression for the dispersion contribution $\Delta\alpha_{\mathrm{disp}}(R)$ to the pair polarizability (second term in (7)) was obtained [13] by relating it to the first-order dispersion energy of a pair of atoms. For consistency with the HFD potentials, a damping of the dispersion terms was introduced with the functions $F(x)$ defined by (10) serving as the damping factors. The adopted form of the collision-induced trace thus was

$$\Delta\alpha(R) = F(R/R_m)\left(\frac{5\gamma C_6}{9\alpha_0^{\mathrm{exp}}}\right) R^{-6} + \Delta\alpha_{\mathrm{scf}}(R)(\alpha_0^{\mathrm{exp}}/\alpha_0^{\mathrm{scf}})^3. \tag{11}$$

Such damping has only minor effect on the final results. For Ne, the unscaled SCF + CI trace tabulated in [15] was used without any additional dispersion term.

The integrals (6) were evaluated numerically by interpolating the values of the $\Delta\alpha(R)$ functions tabulated [15–17] in a limited number of points with the cubic splines, and using the R^{-6} asymptotics at large separations. Calculated $B_\varepsilon = B_\varepsilon(T)$ dependences in the range $T \leq 1400$ K are compared in Fig. 1 (full lines) with the experimental data [5, 7, 25, 26]. Figure 1 also depicts the results [12] (dashed lines) obtained with the (12:6) interaction potential and the static $\Delta\alpha(R)$ functions approximated with (7), where the range parameters $R_t \approx 0.75\, a_0$ have been previously estimated by Proffitt et al. [14] in a study of the polarized collision-induced light scattering (CILS), and the scaling factors λ_t were adjusted to match the room temperature experimental values of B_R measured at 633 nm [27].

We see that in all cases the experimental results indicate steeper temperature variations of B_ε than what is obtained by modelling the trace $\Delta\alpha(R)$ either by (7) or by (11), irrespective of the interatomic potential energy function used in the calculations. Weaker temperature dependence of the calculated B_ε in comparison with the observed one was also noted by Huot and Bose [5].

To get some insight into the nature of a systematic deviation of the computed temperature variation from the behaviour found in experiment, we plotted in Fig. 2 all but the oldest reported data on the dielectric and refractivity virial coefficients in a reduced form as

$$b^*(T^*) = B(T)/(A N_A \sigma^3) \quad \text{vs.} \quad T^* = kT/\varepsilon,$$

where B is B_ε or B_R, A is A_ε or A_R, and σ and ε are the parameters of the HFD potentials. Also shown in Fig. 2 is the sign-inverted reduced *density* virial coefficient $-\mathrm{Const} \cdot B_\varrho^*(T^*) = -0.0190\, B_\varrho(T)/N_A \sigma^3$ as function of the reduced temperature computed with the aid of the HFD potentials and scaled to fit the room temperature b^* data points for xenon [7, 27]. As is evident from Fig. 2, the $b^*(T^*)$ data points group around the scaled $B_\varrho^*(T^*)$ curve in a surprisingly regular manner, moreover, both dependences seem to lead to the Boyle temperature of $T_B^* \approx 2.88$ [1]. In fact, the same tendency persists for the reduced B_R values of molecular gases as well, though introduction of different potential energy functions, particularly anisotropic ones, makes the choice of the reduction parameters rather uncertain. Note that, unlike the two-parameter (12:6) potential, the HFD potentials do not generate a unique reduced $B_\varrho^*(T^*)$ function for different atomic gases. The differences between the individual gases are, however, too small to be made visible on the scale of Figure 2. The reduced Boyle temperature for the (12:6) potential is $T_B^* = 3.42$ [28].

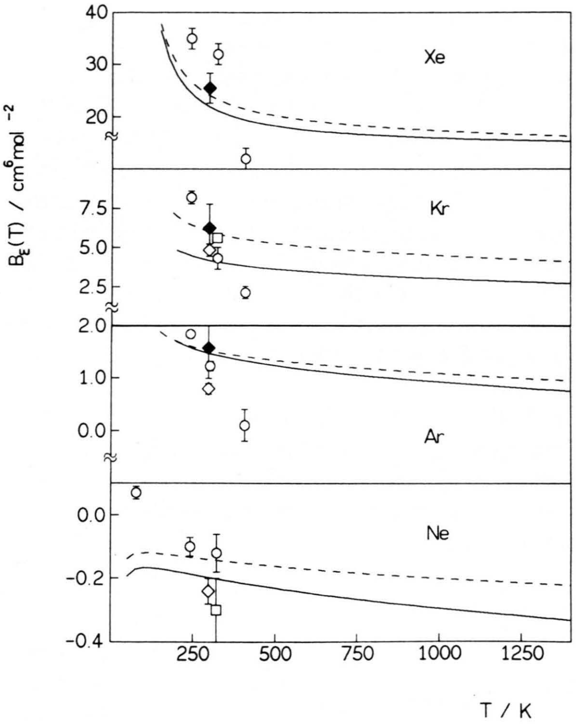

Fig. 1. Temperature dependence of the second dielectric virial coefficient $B_\varepsilon(T)$. ○: [5], □: [25], ◇: [26], ◆: [27] (experimental values). —: calculated this work, - - -: calculated [12].

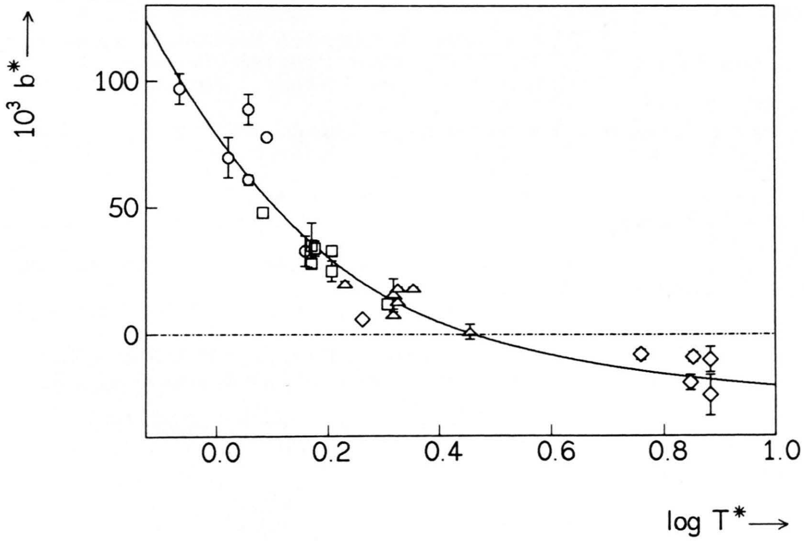

Fig. 2. Temperature dependence of the reduced second dielectric virial coefficient b^*. ◇: Neon; △: Argon; □: Krypton; ○: Xenon. —: calculated reduced second density virial coefficient, this work.

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[1] The coincidence of the Boyle points for $B_\varrho(T)$ and $B_R(T)$ was noted in an analysis of some unpublished refractivity data for neon by Artym et al. [29], who suggested the same should be the case for other gases as well.

One may suspect the remarkably strong correlation between the dielectric and density virial coefficients revealed in Fig. 2 to be an artefact caused by incomplete elimination of the influence of B_ϱ in the practical implementation of the differential expansion technique, see (3). We think that unlikely in view of at least semiquantitative consistency of the reported B_ε and B_R data and the results obtained in the studies of the polarized CILS [14], which is free from interference with the density virial coefficients.

Taken as an empirical fact, the existence of the Boyle point on the $B_\varepsilon(T)$ dependence allows to impose certain restrictions on the collision-induced trace. Similar to the integrand for the second virial coefficient B_ϱ,

$$\begin{aligned} B_\varrho(T) &= 2\pi N_A \int_0^\infty [1-\exp(-V(R)/kT)]\, R^2\, \mathrm{d}R \\ &= 2\pi N_A \int_0^\infty [\exp(V(R)/kT)-1] \\ &\quad \cdot \exp[-V(R)/kT]\, R^2\, \mathrm{d}R, \qquad (12) \end{aligned}$$

the integrand in (6) should also have positive and negative branches, their areas becoming equal at T_B. Indeed, the $\Delta\alpha(R)$ functions for the heavier rare gases computed by Dacre [16, 17], do have profiles resembling the sign-inverted profile of the integrand in (12). However, as suggested by Fig. 1, the short-range negative wells are evidently not deep enough for the appearance of the Boyle point. One can, of course, always find a pair of the fitting parameters λ_t and R_t in the approximation (7) to match a certain data point at one temperature and simultaneously make b^* vanish at the Boyle temperature. For the gases considered here, this leads to unrealistically small range parameters $R_t \approx 0.2-0.3\ a_0$, which would completely destroy any concordance with the polarized CILS.

An obvious conclusion is that (7) should after all be not a good approximation for the incremental trace. Limitations of the trace model (7) have already been emphasized by Proffitt et al. [14]. On the other hand, the scatter of the existing experimental data is still too great to make an attempt of finding an alternative parametrization of the trace meaningful. More theoretical and experimental studies are required for improving the trace models of the collision-induced polarizabilities.

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