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Third Virial Coefficients of Argon from First Principles[†]

Alexandr Malijevský

Institute of Theoretical Physics, Faculty of Mathematics and Physics, Charles University Prague, V Holešovičkách 2, 180 00 Praha 8, Czech Republic and E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Suchbátka, Czech Republic

František Karlický and René Kalus

Department of Physics, University of Ostrava, 30. dubna 22, 701 03 Ostrava 1, Czech Republic

Anatol Malijevský*

Department of Physical Chemistry, Institute of Chemical Technology, 166 28 Prague 6, Czech Republic and Center of Biomolecules and Complex Molecular Systems, Institute of Chemical Technology, 166 28 Prague 6, Czech Republic

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Third virial coefficients of argon have been calculated using a recent ab initio state-of-the-art pair potential and a new ab initio three-body potential. The theoretical results have been compared with experimental data in the range of temperatures from 130 to 673 K. The comparison reveals an excellent agreement between the theoretical and the newest experimental results: For all considered temperatures, differences between the theoretical and the experimental values are within uncertainties of the experimental data. The theoretical third virial coefficients reported in this work are also compared with those obtained using alternative theoretical approaches.

I. Introduction

The goal of the molecular theory is an accurate (quantitative) prediction and interpretation of the properties of macroscopic systems without any adjustable parameters, that is, using only universal constants such as the charge of electron, velocity of light, and the Planck constant. The simplest real systems to reach the goal are rare gases for their sphericity and nonpolarity. Among them, argon is the most suitable for several reasons. First, it is the most experimentally explored rare gas; second, quantum effects at moderate temperatures and pressures are not too important, and third, the number of electrons is a reasonable compromise between helium and xenon, which is important in quantum chemical calculations.

The simplest bulk quantity directly connected with two-body (pair) interactions is the second virial coefficient. Early calculations were based on the Lennard-Jones 12–6 and related potentials. It is well-known that these simple potentials with parameters such as ϵ and σ fit to the second virial coefficient or low-density viscosity data are not sufficiently accurate for a large range of state variables (temperature, density); see, for example, ref 1. Later, more sophisticated empirical and semi-empirical pair potentials with a number of free parameters (their values were obtained by multi-property fits to second virial coefficients, low-density transport properties, spectral data, scattering data, etc.) combined with known dispersion coefficients (C_6 , C_8 , C_{10} , etc.) were proposed.² As a next step, attempts to calculate pair intermolecular potentials ab initio, that is, without any parameter fitted to experimental data, were made; see, for example, ref 3 and references therein.

Pair intermolecular potential is the only input for theoretical calculations of low-density bulk quantities. For a dense gas, liquid, and solid, three-body interactions must be taken into account (see below). It is believed that four-body and higher interactions are not important. Anyway, there are no tools to extract them with a reasonable accuracy using either theoretical methods or experimental data, at present.

The simplest bulk property directly connected with three-body intermolecular interactions is the third virial coefficient, C . It can be written as a sum of three contributions

$$C = C_{\text{add}} + C_{\text{nadd}} + C_{\text{quant}}, \quad (1)$$

where C_{add} is a part of the third virial coefficient calculated using pair intermolecular interactions only, C_{nadd} is a contribution of three-body interactions, and C_{quant} is a quantum correction to the classical third virial coefficient. It holds

$$C_{\text{add}} = -16\pi^2 N^2 r_m^6 \int_0^\infty \int_r^\infty \int_s^{r+s} f(r) f(s) f(t) t \, dt \, s \, ds \, r \, dr \quad (2)$$

$$C_{\text{nadd}} = 16\pi^2 N^2 r_m^6 \int_0^\infty \int_r^\infty \int_s^{r+s} e(r) e(s) e(t) [\exp(-\beta u_3) - 1] t \, dt \, s \, ds \, r \, dr, \quad (3)$$

$$C_{\text{quant}} = N^2 h^2 r_m^4 \beta^2 / (m\epsilon) \int_0^\infty \int_r^\infty \int_s^{r+s} f(s) f(t) e(r) \left(\frac{d^2 u_2}{dr^2} + \frac{2}{r} \frac{du_2}{dr} \right) t \, dt \, s \, ds \, r \, dr. \quad (4)$$

Here, $f(r) = e(r) - 1 = \exp[-\beta u_2(r)] - 1$ is the Mayer function, $u_2(r)$ is the pair potential, $u_3 \equiv u_3(r, s, t)$ is the three-body

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* Corresponding author.

potential, $\beta = 1/k_B T$, r_m is a position of the minimum of the pair potential, ϵ is its depth, m is the mass of the molecule (atom), and N is the Avogadro constant. Variables r , s , t are interparticle distances⁴ reduced by r_m . In eq 4, only quantum corrections to C_{quant} caused by pair interactions are taken into account; three-body corrections have been omitted as they are small. Otherwise, eqs 2–4 are exact in the range of temperatures where the third virial coefficients are measured.

The only inputs to eqs 2–4 are the pair and three-body potentials, $u_2(r)$ and $u_3(r, s, t)$, respectively. The most accurate pair potential of argon is a semiempirical potential of Aziz.⁵ However, present state-of-the-art computational science allows for the calculation of the pair potential for argon with almost the same accuracy from first principles.³

The three-body potential was often ignored in the past; see, for example, ref 1. However, its omission causes serious errors at low and mediate temperatures; see ref 6 and references therein. For example, at $T = 150$ K, the three-body contribution to the third virial coefficient of argon is 30% of the total value.⁷

There are no sufficiently accurate experimental data (virial coefficients, spectral data, transport properties, scattering measurements) which allow for the construction of empirical three-body potentials in the same manner as it has been done for pair potentials.^{2,5} Thus, there remain two routes. The first is based on a truncated dispersion series⁸

$$u_3(r, s, t) = u_3(\text{DDD}) + u_3(\text{DDQ}) + u_3(\text{DQQ}) + u_3(\text{DDO}) + u_3(\text{QQQ}) + \dots \quad (5)$$

where DDD denotes dipole–dipole–dipole interaction, DDQ is dipole–dipole–quadrupole, DDO is dipole–dipole–octupole, and so forth. The triple dipole as represented by Axilrod–Teller–Muto (DDD) term⁹

$$u_3(\text{DDD}) = \frac{\nu(1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3)}{(rst)^3} \quad (6)$$

is often used to model u_3 as it is believed that the higher order terms in the dispersion expansion, DDQ, DQQ, and so forth, fortunately cancel. A disadvantage of the dispersion series is that it diverges at short interparticle distances. It was partially corrected to charge-overlap effects by Varandas.¹⁰

The second route is based on ab initio calculations of u_3 pioneered for neon by Ermakova et al.¹¹ and for argon by Mas et al.¹² by employing their SAPT approach (see ref 13 and references therein) and extended recently to supramolecular calculations by Karlický and Kalus.¹⁴

A problem with the third virial coefficient is that it is difficult to extract its experimental values from volumetric measurements¹⁵ with sufficient precision. Thus, earlier attempts to judge various calculations of the third virial coefficient were inconclusive. Only recently, Tegeler et al.¹⁶ precisely recalculated experimental data of Gilgen et al.¹⁷ These new data help theory to judge more reliably the accuracy of different theoretical approaches.

The aim of this paper is to calculate third virial coefficients of argon using the ab initio pair potential of ref 3 and the new ab initio three-body potential and to compare them thoroughly with available experimental data as well as with earlier theoretical estimates.

II. Theory

The ab initio pair potential of Slavíček et al.³ was used in this work. It was obtained using CCSD(T) all electron calculations

with an extended basis set (aug-cc-pV6Z) combined with bond functions (spdfg). The calculated pair potential was tested on experimental data for the second virial coefficients, spectral characteristics, and scattering data. An excellent agreement between the theoretical and the experimental values was found, similar to that of the semiempirical pair potential of Aziz.⁵ The potential was tested (together with the three-body DDD term) on dense fluid thermodynamic properties,¹⁸ again in accordance with experimental data.

The three-body potential was calculated using the supra-molecular approach, the CCSD(T) correlation method, and the d-aug-cc-pVQZ basis set as implemented in the MOLPRO package.¹⁹ The points included in those calculations cover a broad range of Ar₃ configurations that can be expected in condensed argon. For short interatomic distances, the reliability of the three-body potential is guaranteed up to Ar₃ energies of $\sim 10^4$ cm^{−1}. For long interatomic distances, the calculations were performed so that the potential could be smoothly linked to the asymptotic expansion of eq 5 with the interaction coefficients taken from independent, presently the most accurate ab initio calculations by Thakkar et al.²⁰ Detailed tests we performed for several *D*_{3h} geometries of Ar₃ indicate that the calculations were converged within < 1.0 cm^{−1} for short interatomic distances and within 0.1 – 0.01 cm^{−1} around the equilibrium configuration of Ar₃ or for long interatomic distances, respectively.

A comprehensive description of the ab initio calculations of u_3 as well as details of its analytical representation will be published in a separate paper and is presently available from authors by request. Here, we give only a brief description of the analytical formula used. The calculated points were represented by

$$u_3 = (1 - F_D)u_3^{(\text{SR})} + F_D u_3^{(\text{LR})} \quad (7)$$

where $u_3^{(\text{SR})}$ represents the short-range part, $u_3^{(\text{LR})}$ is the long-range part of the three-body potential, and F_D is a damping function that switches between the two parts of u_3 when going from small to large sizes of Ar₃ and vice versa. The long-range part of eq 7 is represented by a sum of asymptotic dispersion terms of eq 5

$$u_3^{(\text{LR})} = Z_{\text{DDD}}W_{\text{DDD}} + Z_{\text{DDQ}}W_{\text{DDQ}} + Z_{\text{DQQ}}W_{\text{DQQ}} + Z_{\text{DDO}}W_{\text{DDO}} + Z_{\text{QQQ}}W_{\text{QQQ}} \quad (8)$$

with the interaction coefficients, Z_{KLM} , taken from independent ab initio calculations by Thakkar et al.²⁰ and kept constant during the least-squares adjusting of eq 7; the geometry factors, W_{KLM} , are taken from ref 8. The short-range part of eq 7 is represented by²¹

$$u_3^{(\text{SR})}(r, R, \theta_j) = \sum_{i,j,k} C_{ijk} \{1 - \exp[-a_1(r - r_r)]\}^i \{\exp[-a_2(R - R_r)]\}^j L_k(\cos \theta_j), \quad (9)$$

where r , R , and θ_j are the Jacobi coordinates; a_1 , a_2 , r_r , R_r , and C_{ijk} are adjustable parameters, and L_k is the Legendre polynomial of k th order. The damping function, F_D , is a slightly modified damping function used by Aziz et al. for the HFD family of diatomic potentials,²²

$$F_D(\Lambda; \alpha, \beta) = \begin{cases} \exp(-[D(\alpha, \beta)/\Lambda - 1]^2) & \text{for } \Lambda < D(\alpha, \beta), \\ 1 & \text{for } \Lambda \geq D(\alpha, \beta), \end{cases} \quad (10)$$

TABLE 1: Third Virial Coefficients of Argon^a

<i>T</i> /K	<i>C</i> (exp)	<i>C</i> (add)	<i>C</i> (quant)	<i>C</i> (nadd)	<i>C</i> (calc)	<i>C</i> (calc) – <i>C</i> (exp)
130	2232 ± 300	1154	25	1189	2368	135
135	2389 ± 100	1281	15	1073	2369	–20
140	2344 ± 100	1358	12	922	2292	–52
160	2171 ± 100	1411	8	704	2123	–48
170	2053 ± 100	1393	5	592	1990	–63
180	1864 ± 100	1345	3	577	1925	61
190	1718 ± 100	1261	2	486	1749	31
200	1635 ± 100	1205	1	439	1645	10
220	1455 ± 100	1106	1	367	1474	19
250	1292 ± 100	991	1	293	1285	–7
265	1211 ± 100	947	1	267	1214	3
280	1157 ± 100	911	1	244	1156	–1
295	1114 ± 100	880	1	225	1106	–8
310	1052 ± 100	854	0	209	1063	11
325	1034 ± 100	833	0	174	1007	–27
340	1005 ± 100	815	0	183	998	–7
398 ^b	968 ± 100	766	0	148	914	–54
423 ^c	970	753	0	137	890	–80
473 ^d	860	733	0	119	932	72
573 ^d	765	709	0	95	804	39
673 ^d	790	694	0	80	774	–16

^a All contributions are in cm⁶ mol^{–2}. *C*(exp) are experimental values taken from ref 16. ^b Reference 23. ^c Reference 26. ^d Reference 24. *C*(add) is a contribution calculated using the pair potential eq 2; *C*(quant) is a quantum contribution eq 4; *C*(nadd) is a contribution of the three-body interactions eq 3. *C*(calc) = *C*(add) + *C*(quant) + *C*(nadd).

where Λ is the perimeter of the Ar₃ triangle (and represents thus its size), and the adjustable parameter, *D*, depends on the shape of the Ar₃ triangle via a simple polynomial of cosines of two smaller angles in Ar₃, $\alpha \leq \beta$,

$$D(\alpha, \beta) = k_0 + k_1 \cos \alpha + k_2 \cos \beta + k_3 \cos^3 \alpha + k_4 \cos^3 \beta \quad (11)$$

The adjustable parameters of eq 9 were least-squares fit to calculated ab initio points; the parameters of eq 11 were adjusted so that the asymptotic expansion given in eq 8 deviate from the calculated points by less than ~ 0.1 cm^{–1} everywhere $\Lambda \geq D(\alpha, \beta)$. The fit we obtained in this way deviates from the calculated points by ~ 0.2 cm^{–1} and thus preserves the accuracy of the underlying ab initio points.

The new three-body potential is fully compatible with the (usually employed) asymptotic expansion of eq 5 in the long-range region of interatomic distances but deviates significantly from this approximate formula at medium and, in particular, short distances (mostly by several dozens to several hundreds of cm^{–1}). The main distinction from the previously reported ab initio three-body potential for Ar₃ by Lotrich and Szalewicz¹³ consists of different quantum-chemistry methods employed (SAPT vs supramolecular CCSD(T) calculations), different formulas used to represent the ab initio points analytically, and a broader range of Ar₃ configurations used in the present work.

III. Results

Results of our calculations are shown in Table 1. The three-body contributions are particularly large at low temperatures, as can be expected. At *T* = 130 K, they contribute to the total third virial coefficient by 53%. At high temperatures, the three-body contributions are smaller, though not negligible. At *T* = 673 K, they amount to 10% of the total value. For argon, quantum contributions are small even at low temperatures (1% at *T* = 130 K).

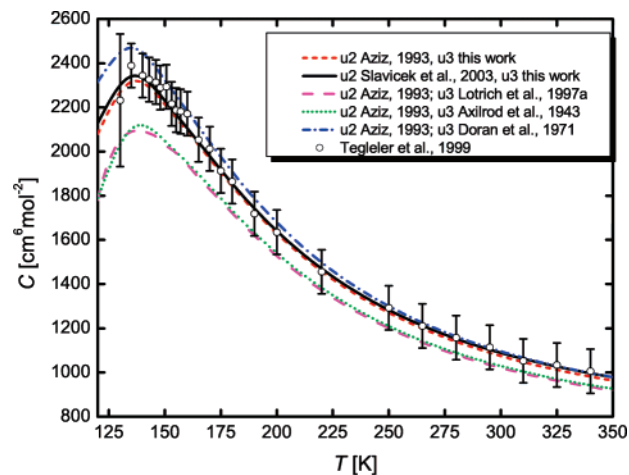


Figure 1. Comparison of theoretical and experimental third virial coefficients of argon. Circles, experimental data of reference;¹⁶ full line, ab initio results of this work; dotted-dashed line, pair potential of Aziz,⁵ three-body potential given by dispersion series (5) up to QQQ; dotted line, pair potential of Aziz,⁵ Axilrod–Teller–Muto (DDD) three-body potential; dashed line, pair potential of Aziz,⁵ three-body potential of Lotrich and Szalewicz¹³ (as reported in ref 12); short dashed line, pair potential of Aziz,⁵ three-body potential of this work.

Comparison with experimental values of ref 16 leads to an excellent agreement. The differences between the present theoretical and the experimental results are much smaller than the estimated uncertainties of the experimental data. This indicates not only the accuracy of the ab initio pair and three-body interatomic potentials but also the fact that the experimental uncertainties are probably slightly overestimated. At temperatures higher than 340 K, the differences between the theoretical and the experimental values are somewhat larger. We believe that this is caused by an insufficient precision of the older experimental data given in refs 23, 24, and 26 as there is no reason to expect a lower accuracy in the theoretical values at higher temperatures. From the theoretical point of view, lower temperatures (around and below the temperature of maximum of *C*) are more interesting because even small deficiencies in pair and three-body potentials are prolonged. For temperatures below 130 K, we are only aware of an old work of Pope et al.²⁵ At temperature 116.4 K, the experimental result is *C* = 1611 cm⁶ mol^{–2}, and the theoretical one is 2030 cm⁶ mol^{–2}. So, they deviate by about 25%. At *T* = 101.2 K, the experimental (–6949) and theoretical (+100) values disagree. This strong disagreement is a challenge both for experiment and for theory.

In Figure 1, the results of this work are further compared with the experimental data and with several theoretical approaches. The present results based on the recent pair and the new three-body ab initio potentials fully agree with the experimental data on the third virial coefficient (as shown in the table), and so do the results based on the Aziz semiempirical pair potential and the new ab initio three-body potential; this is an indirect test of the ab initio pair potential.³ Also, the results obtained using the Aziz potential and truncated dispersion series (DDD + DDQ + DQQ + DDO + QQQ) are very good; they slightly overestimate the data (especially at low temperatures), but still they are within the declared experimental error bars. The results based on the Aziz pair potential, the three-body potential of refs 12 and 13, and the DDD three-body potential somewhat underestimate the experimental values in the region of maximum of the third virial coefficient and are near the borders of error bars at higher temperatures.

IV. Conclusions

Third virial coefficients of argon have been calculated using ab initio state-of-the-art pair and three-body potentials and compared thoroughly with experimental as well as independent theoretical data in a broad range of temperatures (130–672 K). For all of the considered temperatures, the differences between the present theoretical data and the most recent experimental values¹⁶ are fully within declared experimental uncertainties. This seems to indicate a broad reliability of both ab initio potentials used in our calculations, pairwise as well as three-body. A comparison with additional calculations performed for asymptotic expansions (eq 5) clearly shows that the third virial coefficient is rather sensible to the representation of the three-body interactions and that an inclusion of short-range, exchange effects is crucial. Differences observed between the present theoretical values and the data reported for the SAPT three-body potential for argon¹² show that the third virial coefficient is well-suited for testing the accuracy of ab initio three-body calculations.

Argon is a shop-window of the molecular theory of fluids. The present state-of-the-art theoretical chemistry allows quantitative calculations on its low and moderate density thermodynamic properties such as virial coefficients within experimental accuracy. The works on the high-density bulk properties (liquid and crystal quantities) are in progress. The authors believe that it will also be true for other simple atomic as well as molecular systems (Kr, Xe, N₂, O₂, CO, CO₂, etc.) in the near future because of an exponential growth of computer technology. Some promising attempts in this direction have been made by Deiters et al.²⁷ For more complex systems, this is a challenge for the more distant future, however.

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