An \textit{ab initio} nonadditive three-body potential for argon has been developed using quantum-chemical calculations at the CCSD(T) and CCSDT levels of theory. Applying this potential together with a recent \textit{ab initio} pair potential from the literature, the third and fourth to seventh pressure virial coefficients of argon were computed by standard numerical integration and the Mayer-sampling Monte Carlo method, respectively, for a wide temperature range. All calculated virial coefficients were fitted separately as polynomials in temperature. The results for the third virial coefficient agree with values evaluated directly from experimental data and with those computed for other nonadditive three-body potentials. We also redetermined the second and third virial coefficients from the best experimental \( p^p T \) data utilizing the computed higher virial coefficients as constraints. Thus, a significantly closer agreement of the calculated third virial coefficients with the experimental data was achieved. For different orders of the virial expansion, \( p^p T \) data have been calculated and compared with results from high quality measurements in the gaseous and supercritical region. The theoretically predicted pressures are within the very small experimental errors of \( \pm 0.02\% \) for \( p \leq 12 \text{ MPa} \) in the supercritical region near room temperature, whereas for subcritical temperatures the deviations increase up to \( +0.3\% \). The computed pressure at the critical density and temperature is about \( 1.3\% \) below the experimental value. At pressures between 200 MPa and 1000 MPa and at 373 K, the calculated values deviate by 1\% to 9\% from the experimental results. © 2011 American Institute of Physics. [doi:10.1063/1.3627151]

I. INTRODUCTION

The calculation of thermophysical properties from molecular models is of great interest for industrial applications and also for the assessment of theoretical methods. Increasing computational power provides the opportunity to generate molecular models entirely from theory. Especially, the intermolecular pair potential function can be predicted with high accuracy for substances composed of atoms\textsuperscript{1-4} or small molecules, such as carbon dioxide,\textsuperscript{5} methane,\textsuperscript{6} or water,\textsuperscript{7} using quantum-chemical \textit{ab initio} methods. Thermophysical properties calculated with these potentials are, in most cases, reliable only at low densities, in accordance with the fact that the true pair interaction is directly linked to second virial coefficients and transport coefficients of gases in the zero-density limit by means of statistical thermodynamics and kinetic theory.

At higher densities many-body effects have strong influence on macroscopic properties. One way to account for this is the implicit inclusion of many-body effects into the pair potential, which is referred to as the pairwise-additive approach. Typically, these potentials (e.g., the well-established TIP4P water model\textsuperscript{8}) are adjusted to structural information of the molecule and bulk properties, which have been measured in certain limited state regions. Therefore, such a potential is restricted in its predictive capability. The other possibility is to use an explicit nonadditive three-body potential together with a pure pair potential, so that the potential energy of an \( N \)-particle system may be written as

\[
\phi_N = \sum_{i<j} \phi_{ij} + \sum_{i<j<k} \Delta \phi_{ijk},
\]

Axilrod and Teller\textsuperscript{9} as well as Muto\textsuperscript{10} were the first to derive an expression for the nonadditive energy in triplets of atoms by means of perturbation theory of the third order. About fifty years later, accurate calculations of three-body contributions using quantum-chemical \textit{ab initio} methods became feasible. Lotrich and Szalewicz\textsuperscript{11} utilized their symmetry-adapted perturbation theory (SAPT) to develop a nonadditive potential for argon, followed by a three-body potential for neon by Ermakova \textit{et al.}\textsuperscript{12} based on calculations with the fourth-order many-body perturbation theory. Later, Malijevský \textit{et al.}\textsuperscript{13} computed the third virial coefficient of argon applying a new three-body potential, which unfortunately was not discussed in all detail. Recently, Cencek \textit{et al.}\textsuperscript{14} performed \textit{ab initio} calculations up to the full-configuration-interaction (FCI) level to derive the nonadditivity of helium. Three-body potentials of molecules have also been developed, for example, in the case of water using SAPT by Mas \textit{et al.}\textsuperscript{15} and for carbon dioxide by Oakley and Wheatley\textsuperscript{16} applying SAPT and second-order many-body perturbation theory.

The equation of state (EOS) can be obtained from intermolecular potentials either by applying molecular simulation methods, or, for gases and supercritical fluids, by using the
virial expansion:
\[
\frac{P}{\rho k_B T} = 1 + B_2(T) \rho + B_3(T) \rho^2 + \cdots,
\]
where \(P\), \(\rho\), and \(T\) represent pressure, number density, and temperature, respectively, \(k_B\) is Boltzmann’s constant, and \(B_2, B_3, \ldots\) are the virial coefficients. In this paper, we focus on the capabilities, accuracy, and limitations of the virial series. Calculations of second and third virial coefficients are straightforward and have been performed for numerous substances, see, for example, Refs. 6, 17–22. In a comprehensive review on the virial expansion, Masters summarized the developments in theoretical approaches and numerical applications. Most of the theoretical investigations of higher-order virial coefficients were based on the formulations by Mayer or by Ree and Hoover, which have been derived assuming pairwise-additive interactions. Recent progress has been made by Koike and co-workers by introducing the Mayer-sampling Monte Carlo method (MSMC). MSMC refers to an efficient importance sampling Monte Carlo procedure for the computation of the high-dimensional cluster integrals that appear in the formulae for the virial coefficients. It has been applied for the calculation of virial coefficients \(B_n\) up to \(n = 8\) for the Lennard-Jones fluid, up to \(n = 6\) for binary Lennard-Jones mixtures, up to \(n = 6\) for non-polarizable water force fields and alkane models, and up to \(n = 4\) for realistic methanol potentials. However, expressions for nonadditive corrections have been reported only for the third through fifth virial coefficients.

Recently, Hellmann and Bich presented a new derivation of the virial expansion, which is not restricted to pairwise-additive potentials. Furthermore, they provided explicit formulae for the numerical evaluation of the virial coefficients up to \(B_8\) in terms of sums of newly defined cluster diagrams. Since the number of cluster diagrams increases more moderately with increasing \(n\), this approach reduces the computational costs significantly compared to the formulations by Mayer and by Ree and Hoover for \(n \geq 5\) and \(n \geq 6\), respectively.

With the objective of predicting equations of state from \textit{ab initio} interaction potentials, we use argon as model substance, because high-precision experimental data are available for comparison and the most accurate quantum-chemical methods can be applied. In Sec. II, we describe the potential functions utilized in this work, especially the newly developed nonadditive three-body potential. Then in Sec. III, the theoretical aspects concerning the virial expansion, quantum corrections, and the numerical application with MSMC are explained. Section IV presents the results for \(B_3\) through \(B_7\) for the pure \textit{ab initio} two-body potential and for the two-body potential combined with the three-body potential by Axilrod, Teller, and Muto as well as with the new \textit{ab initio} three-body potential. Finally, we compare the obtained values of the different virial equations of state with experimental data for a variety of pressures and temperatures.

II. POTENTIAL FUNCTIONS

A. \textit{Ab initio} pair potential

In preceding papers, we presented a state-of-the-art \textit{ab initio} potential function for the argon atom pair with a well depth of \(\epsilon/k_B = 143.123\) K and related thermophysical properties, such as second acoustic, dielectric, and pressure virial coefficients as well as viscosity and thermal conductivity in the limit of zero density. The comparison of results for the acoustic virial coefficient and for the zero density viscosity with the most accurate experimental data provided particular evidence of the high quality of the potential. Recently, Patkowski and Szalewicz developed a new pair potential for argon. They applied novel families of basis sets in combination with elaborate quantum-chemical methods to estimate the interaction energies and the corresponding errors yielding a potential well depth of 142.944 K. Moreover, they could not reproduce our interaction energies computed with the coupled-cluster method with single, double, and noniterative triple excitations (CCSD(T), Ref. 36) using the d-aug-cc-pV(5+d)Z+(44332) basis set. Consequently, we discovered a mistake in our exponents for the second set of diffuse functions. By recalculating the interaction energies with the corrected quintuple basis set, re-extrapolating the correlation part of the interaction energy to the complete basis set (CBS) limit, and refitting the parameters, we obtained a well depth of 143.017 K. With regard to the interaction energy at the minimum of the potential, both versions of our pair potential and the one by Patkowski and Szalewicz agree within their stated uncertainty.

We also computed values of the second pressure virial coefficient and of the zero-density viscosity for the pair potential by Patkowski and Szalewicz and for our corrected potential function with the same methods as applied in Ref. 19 and compared the results with our previous values. The values of the viscosity coefficient at room temperature calculated for all three potentials differ by less than 0.03% from each other. Compared to the experimental reference data by May et al., the value calculated with the potential by Patkowski and Szalewicz deviates least, however, all theoretically predicted values at room temperature agree with the experimental datum within its standard uncertainty of 0.084%. The same holds for the second virial coefficient, but in contrast to viscosity, the theoretical value for our original pair potential agrees best with the experimental result by Tegeler et al. Therefore, we decided to use the published version of our potential function, which is given by the analytical representation

\[
\phi = A \exp(a_1 R + a_2 R^2 + a_{-1} R^{-1} + a_{-2} R^{-2})
\]

\[
- \sum_{n=3}^{8} C_{2n} \left[ \frac{R^{2n}}{n!} \right] \left[ 1 - \exp(-b R) \sum_{k=0}^{2n} \frac{(b R)^k}{k!} \right].
\]

Here, \(R\) is the distance between two interacting atoms; the parameters can be found in Ref. 3.
B. *Ab initio* nonadditive three-body potential

Following the ideas by Cencek *et al.*\(^{14}\) for helium and Malijevský *et al.*\(^{13}\) for argon, we based our three-body potential for argon on supermolecular coupled-cluster calculations. In this approach, the nonadditive three-body contribution to the interaction energy is readily obtained by

\[
\Delta \phi_{123} = E_{123} - E_1 - E_2 - E_3 - \phi_{12} - \phi_{23} - \phi_{31} = E_{123} + E_1 + E_2 + E_3 - E_{12} - E_{23} - E_{31}. \tag{4}
\]

The energies of the dimers, \(E_1, E_2, E_3, E_{12}, E_{23}, E_{31}\), as well as of the monomers, \(E_1, E_2, E_3\), have to be computed in the full basis set of the trimer to avoid the basis set superposition error, which was demonstrated to be of considerable size for three-body interactions of rare gas atoms by Schwerdtfeger *et al.*\(^ {39}\) In accordance with the *ansatz* by Malijevský *et al.*,\(^{13}\) we used the CCSD(T) method within the frozen-core approximation applying the d-aug-cc-pVQZ basis set by Woon and Dunning.\(^ {40}\) In addition, several other basis sets from the aug-cc-pVXZ (abbreviated as aVXZ), d-aug-cc-pVXZ (daVXZ), t-aug-cc-pVXZ, aug-cc-pV(X+d)Z, and d-aug-cc-pV(X+d)Z series\(^ {40-43}\) with \(X = \{D, T, Q, 5, 6\}\) have been tested for the equilateral triplet configuration with \(R = 7.0\) bohrs. Unfortunately, we found that the trends of the three-body nonadditive energy vary significantly within the different series and from one to another. Hence, we did not extrapolate the correlation contributions to the CBS limit.

So far, three-body effects beyond the CCSD(T) level of theory have only been reported for helium by Cencek *et al.*\(^ {14}\) They revealed that the difference between the three-body nonadditivity computed with the CCSD(T) and the FCI method amounts to up to 12% and is dominated by the contribution resulting from differences between the full iterative and the perturbational treatment of triple excitations at the CCSDT (Ref. 44) and the CCSD(T) levels of theory. In the case of argon, this additional effect was found to be in the same order of magnitude, as can be seen from Table I for the equilateral triplet configuration mentioned above. Due to computational feasibility, we applied the aVTZ basis set in the calculations of \(\Delta \phi^{T−(T)}\) for our three-body potential.

The effect of quadrapole excitations within the coupled-cluster approach has been tested for the representative equilateral triangle (\(R = 7.0\) bohrs) by means of the CCSDT(Q) method\(^ {45}\) with the daVDZ basis set yielding a correction \(\Delta \phi^{Q−T} = 0.052\) K. We considered this effect to be negligible, even though it might be distinctly larger using basis sets of increased size as reported for the pair interaction energy by Patkowski and Szalewicz.\(^ {4}\) Regrettably, such calculations cannot be performed with manageable computational effort these days.

Furthermore, we investigated the influence of relativistic effects within the Cowan-Griffin approximation\(^ {46}\) and the contributions due to core-core and core-valence correlations. Utilizing the aug-cc-pwCVTZ basis set\(^ {47}\) at the all-electron level, the relativistic correction to the three-body nonadditive interaction energy amounts to 0.081 K for the equilateral test configuration, whereas the difference between the all-electron and the frozen-core calculations is 0.022 K. Both effects contribute less than 2% to the nonadditivity for the test geometry and have been neglected in the calculation of the three-body potential. Hence, the total *ab initio* three-body nonadditivity for our potential is given by

\[
\Delta \phi^{tot} = \Delta \phi^{CCSD(T), daVQZ} + \Delta \phi^{T−(T), aVTZ}. \tag{5}
\]

A grid of 228 configurations was chosen, where each triangle was defined by two interatomic distances, \(R_{12}\) and \(R_{31}\), and the enclosed angle \(\theta_1\). This includes 12 equilateral configurations with 4.5 bohrs \(\leq R \leq 15.0\) bohrs, 44 isosceles configurations with 4.5 bohrs \(\leq R_{31} = R_{12} \leq 15.0\) bohrs and \(\theta_1 = \{90°; 120°; 150°; 180°\}\), and 173 scalene configurations with 4.5 bohrs \(\leq R_{31} < R_{12} \leq 15.0\) bohrs and \(\theta_1 = \{90°; 120°; 150°; 180°\}\). All quantum-chemical calculations have been performed using the CFOUR program package\(^ {48}\) except for the trial computations with the CCSDT(Q) method, for which the MRCC code\(^ {49}\) was employed. The geometries and the *ab initio* results can be found in the supplementary material.\(^ {50}\)

Our analytical representation of the potential is given by the sum of an exponential contribution, \(\Delta \phi^{exp}\), and of a damped third-order dispersion term, \(\Delta \phi^{disp, 3}\). With this approach, we followed Malijevský *et al.*\(^ {13}\) and omitted additional fourth-order terms of the multipolar expansion, which have been used by Lotrich and Szalewicz\(^ {11}\) as well as by Cencek *et al.*\(^ {14}\) Similar to Refs. 11 and 14, the short-range part of the potential is represented as

\[
\Delta \phi^{exp}(R_{12}, R_{23}, R_{31}) = \sum_{0 \leq \theta_{1,2,3} \leq 6} A_{k_1k_2k_3} \times \exp[-\alpha_{k_1k_2k_3}(R_{12} + R_{23} + R_{31})] \\
	imes \mathfrak{P}[P_1(\cos \theta_{1}), P_2(\cos \theta_{2}), P_3(\cos \theta_{3})]. \tag{6}
\]

where the operator \(\mathfrak{P}\) sums up the six possible terms that result from the permutation of the interior angles \(\theta_1, \theta_2\), and \(\theta_3\); \(P_k\) refers to the Legendre polynomial of the \(k\)th order. Long-range interactions are represented by the third-order damped asymptotic expansion

\[
\Delta \phi^{disp, 3}(R_{12}, R_{23}, R_{31}) = \sum_{0 \leq \theta_{1,2,3} \leq 6} \sum_{i,j,l} D_{i,j,l}^{\beta}(R_{12}, R_{23}, R_{31}) \\
\times W_{i,j,l}^{(3)} Z_{i,j,l}^{(3)}, \tag{7}
\]
in accordance with Refs. 11 and 14. The prime in Eq. (7) indicates that the term with \((l_1l_2l_3) = (123)\) and its permutations are not considered in the sum. The damping function is defined as

\[ D(\beta_{1l_2l_3}, R_{12}, R_{23}, R_{31}) = D(\beta_{1l_2l_3}, R_{12})D(\beta_{1l_2l_3}, R_{23}) \\
\times D(\beta_{1l_2l_3}, R_{31}), \]

where the factors are given by the Tang-Toennies damping function^{31}

\[ D(\beta_{1l_2l_3}, R_{ij}) = 1 - \exp(-\beta_{1l_2l_3}R_{ij}) \sum_{n=0}^{n_{ij}} \binom{\beta_{1l_2l_3}R_{ij}}{n} \]

Here, \(n_{ij}^{l_1l_2l_3}\) represents the inverse power to which \(R_{ij}\) is raised in the respective angular function \(W_{l_1l_2l_3}^{(3)}\). The leading term with \(l_1 = l_2 = l_3 = 1\) is the triple-dipole term, which is given by

\[ W_{111}^{(3)} = 3(R_{12}R_{23}R_{31})^{-3}(1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3). \]

Explicit formulæ of the other geometrical factors have been derived by Bell,^{32} and by Doran and Zucker,^{55} they are given in the supplementary material. In contrast to the former three-body potentials, we treated the asymptotic coefficients \(Z_{l_1l_2l_3}^{(3)}\) as free parameters of the fit.

The 56 parameters of our potential were determined by successively adding the terms of Eqs. (6) and (7) in the least-squares fitting procedure. They are collected in the supplementary material. Fitted and \textit{ab initio} nonadditive three-body energies agree within 2\% for most configurations, except for some very large and very small triangles as well as for geometries, where the potential function changes its sign. In Figs. 1 and 2, we compare the results of the \textit{ab initio} calculations with the fitted \textit{ab initio} three-body potential and with the widely-used Axilrod-Teller-Muto (ATM) potential^{9,10} for equilateral and symmetric linear configurations. The ATM potential, whose angular function is identical to that of the triple-dipole term, was calculated utilizing Eq. (10) with the prefactor of 3 replaced by the nonadditivity coefficient of \(5.315 \times 10^{-4} \text{ K nm}^{-3}\) given by Sadus and Prausnitz.\textsuperscript{54} As expected, the new \textit{ab initio} three-body potential agrees with the ATM approach for large geometries and shows different behavior for small ones, where the nonadditive interaction cannot be described by dipolar interactions alone.

### III. VIRIAL EXPANSION

#### A. Theory

Mayer\textsuperscript{24} was the first to derive a scheme for the generation of explicit formulæ for pressure virial coefficients \(B_n\) from the canonical partition function assuming pairwise-additive interactions between classical particles. In this approach, graph theory is utilized to obtain expressions for the virial coefficients as integrals of combined (two-particle) Mayer functions \(f_{ij} \equiv \exp(-\phi_{ij}/k_B T) - 1\). Later, Ree and Hoover\textsuperscript{25} reduced the number of necessary graphs by introducing another type of functions \(e_{ij} \equiv f_{ij} + 1 = \exp(-\phi_{ij}/k_B T)\). According to this \textit{ansatz}, the additive contributions to the classical third and fourth virial coefficients are given by

\[ B_{3,\text{add}}(T) = \frac{-1}{3V} \int \cdots \int f_{12}f_{13}f_{23}d\mathbf{R}_1d\mathbf{R}_2d\mathbf{R}_3, \]

\[ B_{4,\text{add}}(T) = \frac{-1}{8V} \int \cdots \int [-2f_{12}f_{13}f_{14}f_{23}f_{24}f_{34} \\
+ f_{12}f_{14}f_{23}f_{34}e_{13}e_{24} + f_{13}f_{14}f_{23}f_{24}e_{12}e_{34} \\
+ f_{12}f_{13}f_{24}f_{34}e_{14}e_{23}]d\mathbf{R}_1d\mathbf{R}_2d\mathbf{R}_3d\mathbf{R}_4. \]
numerical performance. For the fifth virial coefficient, we proceeded in a similar way; the schematic formula can be found in Ref. 25.

Expressions for nonadditive three-body contributions to the classical third and fourth virial coefficients were derived by Johnson and Spurling as

$$B_{3,\text{add}}^\text{cl}(T) = -\frac{1}{3V} \int \cdots \int \left[ \exp \left( -\frac{\Delta \phi_{123}}{k_B T} \right) - 1 \right] e_{12} e_{13} e_{23} e_{24} e_{34},$$

$$B_{4,\text{add}}^\text{cl}(T) = \frac{1}{8V} \int \cdots \int \left[ \exp \left( -\sum_{i<j<k} \frac{\Delta \phi_{ijk}}{k_B T} \right) - 1 \right] e_{12} e_{13} e_{14} e_{23} e_{24} e_{34},$$

The respective relation for the fifth virial coefficient is given in Ref. 34. At low temperatures, the assumption of classical particles is no longer valid. However, if the system under study is not too far from classical conditions, quantum effects may be treated as quantum corrections to the classical value of any thermodynamic property. According to McQuarrie, the configuration integral $Z_N$ for $N$ monatomic particles applying the first-order quantum correction is given as

$$Z_N = \int \cdots \int \exp \left( -\frac{\phi_N}{k_B T} \right) \left[ 1 - \frac{\hbar^2}{12m(k_B T)^2} \sum_{k=1}^N \left( \nabla_k^2 \phi_N - \frac{1}{2k_B T} \left( \nabla_k \phi_N \right)^2 \right) \right] d\mathbf{R}_1 \cdots d\mathbf{R}_N,$$

where $m$ is the average atomic mass of argon and $\hbar$ is Planck’s constant divided by $2\pi$. This leads to a simple expression for the second virial coefficient (see, also Ref. 56)

$$B_2^{\text{cl+qc}}(T) = -\frac{1}{2V} \int \int (f_{ij} - q_{ij}) d\mathbf{R}_1 d\mathbf{R}_2$$

with

$$q_{ij} = \frac{\hbar^2}{12m(k_B T)^2} \exp \left( -\frac{\phi_{ij}}{k_B T} \right) \left( \phi_{ij}'' + \frac{2}{R_{ij}} \phi_{ij}' \right),$$

where $\phi_{ij}'$ and $\phi_{ij}''$ represent the first and the second derivative of the pair potential with respect to the interatomic distance $R_{ij}$. For $B_{3,\text{add}}$ and $B_{4,\text{add}}$, we derived formulae including quantum corrections by an analogous approach. Starting from the Ree-Hoover expressions [Eqs. (11) and (12)], all $f_{ij}$-functions and all $e_{ij}$-functions have to be dropped, since they belong to higher-order quantum corrections. Thus, the third virial coefficient including the first-order quantum correction is formulated as

$$B_{3,\text{add}}^\text{cl+qc}(T) = -\frac{1}{3V} \int \cdots \int \left[ f_{12} f_{13} f_{23} - q_{12} f_{13} f_{23} ight. \left. - f_{12} q_{13} f_{23} - f_{12} f_{13} q_{23} d\mathbf{R}_4 d\mathbf{R}_5 d\mathbf{R}_6. \right.$$
By calculating the third and the fourth virial coefficients for the Lennard-Jones (12-6) potential, we confirmed that Eqs. (18) and (19) are equivalent to former formulations by Kim and Henderson\textsuperscript{57} as well as by Ram and Singh.\textsuperscript{30} For the virial coefficients beyond \(B_4\), the quantum corrections were neglected, since these virial coefficients do not contribute significantly at low temperatures, at which the quantum corrections are of importance.

At very low temperatures, the first-order quantum correction of the nonadditive contribution to the third virial coefficient, \(B_{3,\text{nadd}}^{\text{qc}}\), needs to be considered. The respective formula was derived in Ref. \textsuperscript{59} by Monago.

Very recently, Hellmann and Bich\textsuperscript{35} have presented a new systematic approach for the calculation of classical virial coefficients based on the expansion of the grand canonical partition function in powers of the activity. This idea, first studied by Mayer,\textsuperscript{60} was developed further to enable numerical computation of high-order virial coefficients for nonadditive potential models. Hellmann and Bich gave expressions for the integrands of the virial coefficients up to \(B_8\) in terms of a new graphical scheme. Even for pairwise-additive potentials, their approach is regarded to be computationally more efficient than the previous formulation by Ree and Hoover for \(n \geq 6\). Due to the large number of terms in the equations for \(B_6\) and \(B_7\), we refer to Ref. \textsuperscript{35} for the explicit expressions.

### B. Numerical application

All contributions to the third virial coefficient, \(B_{3,\text{cl}}^{\text{cl+qc}}\), \(B_{3,\text{nadd}}^{\text{cl}}\), and \(B_{3,\text{nadd}}^{\text{qc}}\) have been calculated by standard numerical integration for temperatures between 83 K and 10 000 K. For this purpose, Eqs. (13) and (18) were modified in such a way that the nine-dimensional integration is replaced by an equivalent three-dimensional one, i.e., the integration variables are transformed as

\[
dR_1 dR_2 dR_3 \rightarrow V dR_1 dR_2 dR_3 \rightarrow V 8 \pi^2 R_1^2 R_2^2 R_3^2 dR_1 dR_2 dR_3 d \cos \theta_1.
\]

However, the dimensionality of the integrals increases strongly with the order of the virial coefficients so that standard numerical integration methods cannot be used efficiently for higher virial coefficients. Hence, we employed the MSMC method\textsuperscript{30} for the evaluation of the integrals for the fourth through seventh virial coefficients. In this procedure, a biased \(n\)-particle Monte Carlo simulation is performed for each virial coefficient \(B_n\). The importance sampling is achieved by using a sampling distribution \(\pi\) which is equal to the absolute value of the integral \(B_n\) of the considered virial coefficient, i.e., a trial move in the MC simulation is accepted with the probability \(\min(1, \pi_{\text{new}} / \pi_{\text{old}})\). The value of the virial coefficient is then obtained using a formula taken from free-energy perturbation methods:\textsuperscript{61}

\[
B_n(T) = B_n^{\text{hs}}(\pi_{\text{new}} / \pi)_{\pi}. 
\]

Here, the superscript \(\text{hs}\) indicates that the hard-sphere fluid was chosen as reference system. The angle brackets represent the simulation averages of the weighted integrands of the realistic potential model, \(\pi_{\text{new}}(T) / \pi\), and the hard-sphere potential, \(\pi_{\text{new}} / \pi\), both computed for the same configurations of the particles according to the sampling distribution \(\pi\). Reference values for the hard-sphere virial coefficients were taken from Ref. \textsuperscript{62}.

Kofke and co-workers\textsuperscript{26,29} utilized only ring-shaped clusters in the integrand of the reference system. However, we found it convenient to use the complete hard-sphere virial coefficient and the respective integrand. Following Singh and Kofke,\textsuperscript{26} the hard-sphere diameter was chosen as the collision diameter \(\sigma\) of the \textit{ab initio} two-body potential (3.36 Å). We further modified the original approach by introducing multi-temperature simulations as suggested in the outlook of Ref. \textsuperscript{26}. Provided that the sampling distribution at a reference temperature, \(T_{\text{ref}}\), is valid for a certain temperature range, the virial coefficients may be calculated for several temperatures in this region with only one simulation, leading to a considerable reduction of the computational costs. Temperature ranges, numbers of temperatures, and reference temperatures of the simulations used in this work are summarized along with other simulation parameters in Table II.

The step sizes in the MC moves were adjusted in short equilibration periods to achieve acceptance rates of 50%. We avoided any unphysical values of the two-body potential at very short interatomic distances by applying a hard-sphere core for \(R < 1.8\) Å. By contrast, the three-body potential, \(\Delta\phi_{ijk}\), was set to zero if at least one of the three distances was smaller than 2.25 Å or larger than 20 Å. Our MSMC code uses simple parallelization by performing independent simulations with the same parameters on 4 to 16 CPU cores and averaging the results.

### IV. RESULTS AND DISCUSSION

#### A. The virial coefficients and their fits

The values for the second virial coefficient, calculated as sum of the classical contribution and quantum corrections up to the third order, were taken from Ref. \textsuperscript{19}.

The virial coefficients \(B_1\) to \(B_6\) were calculated in the aforementioned temperature regions applying the following three interaction models:

- \textit{ab initio} pair potential of Ref. \textsuperscript{3} (denoted by “add”),
- \textit{ab initio} pair potential of Ref. \textsuperscript{3} and three-body interaction according to Axilrod, Teller, and

**Table II.** Temperature ranges and reference temperatures (in K) for the virial coefficients calculated with MSMC. \(N_{\text{temp}}\), \(N_{\text{ran}}\), and \(N_{\text{steps}}\) are the number of temperatures, the number of independent simulation runs, and the number of MC steps per simulation run, respectively.

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>(T_{\text{ref}})</th>
<th>(N_{\text{temp}})</th>
<th>(N_{\text{ran}})</th>
<th>(N_{\text{steps}})</th>
</tr>
</thead>
</table>
The third virial coefficient of argon

B. The third virial coefficient of argon

As already stated, third virial coefficients can serve for the assessment of the quality of nonadditive three-body potentials. However, the determination of third virial coefficients from \(ppT\) measurements is afflicted with large uncertainties. Michels et al.\(^{63,64}\) deduced third virial coefficients of argon from isothe rmal measurements of volume and pressure. Subsequent investigations by Crain and Sonntag,\(^{65}\) by Kalfoglou and Miller,\(^{66}\) as well as by Blancett et al.\(^{67}\) were based on the Burnett method. The most precise \(ppT\) data were determined by Gilgen et al.\(^{68}\) using a two-sinker densimeter. However, the derived values of the third virial coefficient were not in agreement with former studies, since the simultaneous fit of the equation of state as function of density and temperature introduced small errors into the evaluation of the virial coefficients. Therefore, Tegeler et al.\(^{38}\) re-evaluated the second and third virial coefficients by separate analyses of the isotherms.

Errors in the third virial coefficient obtained from \(ppT\) measurements may arise either from the neglect of higher virial coefficients (see, for example, Tegeler et al.\(^{38}\)) or, if the analysis of the isotherm includes further higher virial coefficients, from the loss of physical meaning of these coefficients. The latter issue is demonstrated in Table III by comparison of the virial coefficients \(B_2\) to \(B_7\) at 223.15 K and 273.15 K determined by Blancett et al.\(^{67}\) with the respective values from theory. Second and third virial coefficients are characterized by fair agreement, whereas the higher virial coefficients from Ref. 67 can serve only as fit parameters. Hence, it is advisable to utilize the new theoretical values of the higher virial coefficients to revise the determination of \(B_3\) from experimental data.

As the measurements by Gilgen et al.\(^{68}\) were assessed to be the most accurate \(ppT\) data available for gaseous and supercritical argon, we reanalyzed these data as follows. The isothermal fits were performed according to the same orders of the virial expansion as indicated by the temperature ranges of the theoretical calculations (see Table II). For temperatures below 140 K, \(B_4\) was fixed at the theoretical value calculated using the new \(ab\ initial\) three-body potential, whereas \(B_4\) was considered as fit parameter at higher temperatures. For 140 K \(\lesssim T < 146\) K, only \(B_5\) was taken from theory, while for higher temperatures, the theoretical values of \(B_5\), \(B_6\), and \(B_7\) were used as constraints. All reevaluated second and third virial coefficients are given in the supplementary material.\(^{50}\)

In Fig. 3, the experimentally obtained third virial coefficients are presented together with values computed for the three models described in Sec. IV A as well as for the nonadditive three-body potentials by Lotrich and Szalewicz\(^{11}\) and by Malijevský et al.\(^{13}\) The reanalyzed data show considerably smaller values compared to the data by Tegeler et al.\(^{38}\) being outside the error bars given in Ref. 38 for temperatures below 155 K. However, there is striking agreement with the theoretical values calculated with the new \(ab\ initial\) nonadditive three-body potential (see Fig. 3b) for a deviation plot). Moreover, the re-evaluation yielded values of the second virial coefficient which are in better agreement with the theoretical values from Ref. 19 compared with the previous results by Tegeler
The results for the virial equation of state are discussed with regard to the convergence of the series expansion and to the different interaction models. For this purpose, we again compare with the highly accurate \( p_0T \) measurements by Gilgen et al., performed in the temperature range from 90 K to 340 K and for pressures up to 12 MPa. These data are characterized by a relative uncertainty in density of \( \pm 0.02\% \), except for \( 150.7 \text{ K} \leq T \leq 170 \text{ K} \), where the uncertainty was given in terms of pressure as \( \pm 0.01\% \) to \( \pm 0.02\% \). Regardless of the chosen physical quantity in Ref. 68, we estimate the uncertainty in pressure to be \( \pm 0.01\% \) to \( \pm 0.02\% \) for the entire temperature range of the experiments.

In Fig. 4, the convergence behavior of the virial equation of state is illustrated for the interaction model nadd-new including the \( \text{ab initio} \) two-body potential and the \( \text{ab initio} \) three-body nonadditivity. Generally, the deviations of the calculated values from the experimental data decrease by successively adding terms of the virial series up to \( B_3 \). With inclusion of \( B_6 \) and \( B_7 \), the situation is different for the temperatures considered. For the highest temperature of the measurements \( [T = 340 \text{ K}, \text{ see Fig. 4(d)}] \), the virial coefficients beyond \( B_5 \) yield no significant improvement, corresponding to the fact that already the series up to \( B_5 \) gives pressures within the uncertainty of the experiment. At 200 K, \( B_6 \) improves the agreement due to its large relative uncertainty associated with a change of sign in that temperature region. For the critical isotherm [see Fig. 4(b)], the virial series up to \( B_6 \) gives the best agreement with the experimental data corresponding to a close-by zero crossing of \( B_7 \). In the subcritical gaseous region, ordinary convergence behavior is observed for densities up to the saturated vapor densities accompanied by rather large uncertainties due to the limitations of the theoretical calculations.

The influence of the interaction model on the virial equation of state is demonstrated in Fig. 5. Since the seventh virial coefficient has only been computed for the nadd-new model, we compare the results including the virial coefficients up to \( B_6 \). As expected, the calculated pressures deviate clearly from the experimental data in the whole temperature range if non-additive contributions to the interatomic interactions are neglected. Although the effect of the nonadditive potential on the third virial coefficient is quite similar for the nadd-ATM and nadd-new models (see Sec. IV B), the comparison of the complete virial equations of state reveals significant differences. For \( T = 146 \text{ K} \) and \( T = 340 \text{ K} \), both models result in similar deviations from the experimental data, albeit with different sign. In contrast, for the intermediate temperatures, the \( \text{ab initio} \) nonadditive three-body potential leads to considerably better agreement as demonstrated in Figs. 5(b) and 5(c). For the critical temperature and density (535.6 kg m\(^{-3}\)), the deviation of the calculated pressure from the experimental value of the critical pressure determined by Teget et al. reduced from 3.1\% to 1.1\% when using the \( \text{ab initio} \) three-body nonadditive potential instead of the Axilrod-Teller-Muto potential. However, both virial equations of state fail to predict the pressures of critical and near-critical argon at higher densities, since clusters consisting of far more than six argon atoms coincide perfectly with our model at temperatures above 200 K, whereas at lower temperatures, they are closer to the values obtained for the model by Lotrich and Szalewicz. Their three-body potential gives values for the third virial coefficient that are larger than our results over the whole temperature range, in contrast to the ATM potential, which gives slightly smaller values.

The difference between results computed with the new \( \text{ab initio} \) nonadditive three-body potential and with the previous potentials is probably due to the improved quantum-chemical method (CCSDT). Even though we did not include further corrections to the \( \text{ab initio} \) three-body nonadditivity, the theoretically calculated third virial coefficients and the re-evaluated values from experiment show a satisfactory consistency.
FIG. 4. Relative deviations of the calculated pressures (nadd-new) for different orders of the virial expansion from the experimental data by Gilgen et al. (Ref. 68). Connecting lines are given for clarity. ———, ideal gas; ▲——▲, virial expansion up to $B_2$; ▼——▼, up to $B_3$; ◦——◦, up to $B_4$; △——△, up to $B_5$; □——□, up to $B_6$; ×——×, up to $B_7$.

The $p\rho T$ measurements by Gilgen et al. were performed only at low and medium pressures up to 12 MPa. To validate further the $ab$ initio equation of state, a comparison is advisable for supercritical argon at higher pressures. Tegeler et al.38 assessed the $pVT$ data by Robertson et al.69 to be of high accuracy at pressures up to 1000 MPa. In Fig. 6, the convergence of the $ab$ initio virial equation of state is illustrated for $T = 373.15$ K. The deviations of the calculated pressures including virial coefficients up to $B_7$ from the experimental data range from 0.8% at the lowest density to 9.3% for the highest one. Moreover, at the highest densities, the deviations are smaller if $B_7$ is omitted in the calculation of the pressure. But this does not necessarily impair the quality of the seventh virial coefficient, as $B_8$ can be expected to be negative. The value of $B_8$ was estimated to be $-7.9 \times 10^8$(cm$^3$mol$^{-1}$)$^7$ by converting the approximate value computed for the Lennard-Jones potential by Schultz and Kofke27 with the standard parameters $\sigma = 3.4$ Å and $\epsilon/k_B = 120$ K. Using this value yields a noticeable decrease of the deviation. However, this represents only a rough estimation, since the Lennard-Jones values were reported to be afflicted with uncertainties in the order of the value of the eighth virial coefficient.

V. SUMMARY AND CONCLUSIONS

A new nonadditive three-body potential for argon has been developed based on supermolecular $ab$ initio calculations at the CCSD(T) level of theory. We also included a correction term for the next higher coupled-cluster approach, CCSDT, as it contributes considerably to the nonadditive energy. An analytical potential function with 56 parameters was fitted to the $ab$ initio results.

Virial coefficients up to $B_7$ were calculated for wide temperature regions utilizing the Mayer-sampling Monte Carlo approach by Kofke and co-workers. The computations were based on the formulation of the integrands by Ree and Hoover for the virial coefficients up to $B_5$. Expressions for the determination of virial coefficients for $n > 5$ including nonadditive interactions were not available in previous studies. Recently, Hellmann and Bich provided such formulae in terms of a graphical scheme. Therefore, our results for argon
FIG. 5. Relative deviations of the pressures calculated for different interaction models from the experimental data by Gilgen et al. (Ref. 68). The virial equation of state includes all terms up to \( n = 6 \). Connecting lines are given for clarity. ‡—‡, add; ■—■, nadd-ATM; □—□, nadd-new.

FIG. 6. Relative deviations of the calculated pressures (nadd-new) for different orders of the virial expansion from the high pressure experimental data by Robertson et al. (Ref. 69). Connecting lines are given for clarity. •—•, ideal gas; ▲—▲, virial expansion up to \( B_2 \); ▼—▼, up to \( B_3 \); ○—○, up to \( B_4 \); △—△, up to \( B_5 \); □—□, up to \( B_6 \); ×—×, up to \( B_7 \); ◦—◦, up to \( B_8 \) with an estimated value of \( B_8 \) taken from Lennard-Jones results in Ref. 27.

also represent a verification of their theoretical formulations. Furthermore, quantum corrections to the virial coefficients have been considered up to \( B_4 \). For all calculations, the highly accurate \textit{ab initio} pair potential developed in a preceding work was applied. In order to investigate the influence of the interaction model, we calculated the virial coefficients not only for the total \textit{ab initio} three-body potential, but also for the pure pairwise-additive model and for the combination of the \textit{ab initio} two-body potential with the empirical three-body potential by Axilrod, Teller, and Muto. The resulting virial equations of state were given as polynomials in the reduced temperature for each virial coefficient.

Utilizing the higher virial coefficients calculated in this work, we performed a new analysis of the precise \( p \rho T \) measurements by Gilgen et al. to derive improved values of the second and third virial coefficients. The resulting values agree remarkably well with our theoretical predictions. However, some data computed for two previous \textit{ab initio} three-body potentials and also some experimental results disagree slightly with our values. Hence, further theoretical investigations are desirable to reduce the uncertainty of the three-body nonadditivity.
The pressures calculated from the ab initio virial equation of state exhibit smaller deviations from the best experiments than the values computed for the empirical nonadditive three-body potential by Axilrod, Teller, and Muto. For temperatures far above the critical temperature, the theoretically predicted values agree with the experimental data by Gilgen et al. within the uncertainty of the measurements. In the range of small to medium pressures, the virial coefficients beyond $B_3$ do not contribute significantly to the pressure. However, for higher pressures, $B_5$ to $B_7$ have to be considered to achieve agreement with the experimental data. In the critical and near critical region, the results for the pressure concur with the experimental data for densities up to the critical density. As expected, the virial equation of state cannot describe the thermodynamic properties for higher densities at these temperatures. In the subcritical gaseous region, the theoretical results agree with the experimental data and only small deviations are observed due to the uncertainties of the interaction potentials and of the numerical computations.

The method for the calculation of classical virial coefficients including nonadditive interactions can easily be transferred to small molecules. Hence, if accurate two-body and three-body potentials are available, the virial expansion may be used to predict the equation of state for substances that are difficult to handle in experiments, such as toxic or corrosive compounds. Furthermore, theoretical results can serve for the extrapolation of experimental data to high temperatures. Generally, realistic intermolecular potentials (including nonadditivity) represent an alternative to simple force fields, since both microscopic and macroscopic behavior is modelled with improved reliability.

ACKNOWLEDGMENTS

One of us (B. J.) would like to thank the Studienstiftung des deutschen Volkes for financial support.