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Anomaly in the Virial Expansion of IAPWS-95 at Low Temperatures

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Abstract

In the standard reference equation of state for the thermodynamic properties of water, known as IAPWS-95, the fourth virial coefficient $D(T)$ becomes abnormally large in magnitude at temperatures below approximately 300 K. At conditions where a virial expansion using only second and third virial coefficients should be essentially exact (such as vapors at pressures near 100 Pa or 1000 Pa), such a truncated expansion may miss on the order of 2 % of the deviation from ideal-gas behavior in the compressibility factor or the fugacity. The term in IAPWS-95 that causes this issue is identified, and suggestions are made for future equation-of-state development.

Keywords

fugacity; virial coefficients; water

1 Introduction

International standards for thermophysical properties of water are set by the International Association for the Properties of Water and Steam (IAPWS). The current formulation for the thermodynamic properties of water for general and scientific use is given in the Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [1], which was documented in a paper by Wagner and Pr [2]. This widely used formulation is commonly referred to as IAPWS-95.

The IAPWS-95 formulation is relatively complex, consisting of an ideal-gas part plus 56 terms of various types for the reduced residual Helmholtz energy $\phi(\delta, \tau) \equiv \bar{a}/R_w T$, where $\bar{a}$ is the specific residual Helmholtz energy (difference between the Helmholtz energy and that of the ideal gas at the same density ρ and absolute temperature T) and R_w is a mass-based gas constant for water (0.461 518 05 kJ·kg⁻¹·K⁻¹ as given in [1, 2]). δ is the reduced density ρ/ρ_c and τ is the reduced reciprocal temperature T_c/T , where the subscript c indicates the value of the property at the vapor-liquid critical point. For water, $\rho_c = 322$ kg·m⁻³ (in molar units 17 873.728 mol·m⁻³) and $T_c = 647.096$ K. All thermodynamic properties can be

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obtained from the full potential $\phi(\delta, \tau)$ by appropriate differentiation and combination of derivatives [2, 3].

The complexity of the IAPWS-95 thermodynamic potential makes it inconvenient and/or impractical for some purposes, so it is desirable to develop simpler approximations where possible. For the vapor phase at low and moderate pressures, a simple and rigorous expression for thermodynamic properties arises from the virial expansion, where properties are expanded in powers of density (or pressure) around the ideal-gas limit. In the more familiar density form of the virial expansion, the compressibility factor Z is written as

$$Z \equiv \frac{p}{\rho RT} = 1 + B(T)\rho + C(T)\rho^2 + D(T)\rho^3 + \dots, \quad (1)$$

where p is the pressure, ρ is the molar density, and R is the molar gas constant. The second virial coefficient B , a function only of temperature for a given substance, is rigorously related to the interactions between pairs of molecules; C and D similarly arise from interactions among three and four molecules, respectively. At pressures near and below atmospheric, Eq. (1) converges quickly, so in practice the $D(T)$ term is seldom needed and often only the first-order $B(T)$ correction is necessary. Other thermodynamic properties are obtained by differentiation and integration; for example, for a pure component the fugacity coefficient ϕ can be obtained by [4]

$$\ln \phi = \int_0^p \frac{Z - 1}{p} dp = B'p + \frac{C'p^2}{2} + \frac{D'p^3}{3} + \dots, \quad (2)$$

where we have switched from the density form of Eq. (1) to an expansion in pressure which is more convenient for this purpose; the pressure-series virial coefficients are rigorously related to their density-series counterparts [4]:

$$B' = \frac{B}{RT}; \quad C' = + \frac{C - B^2}{(RT)^2}; \quad D' = \frac{D - 3BC + 2B^3}{(RT)^3}. \quad (3)$$

A recent example of the use of virial coefficients to provide simpler calculations is the work of Feistel et al. [5], who described the fugacity of gas-phase air-water mixtures with a virial expansion truncated after the C terms. As part of that work, explicit expressions were presented for $B(T)$ and $C(T)$ for pure water derived from IAPWS-95. Recently, during work toward new correlations for humidity metrology that may replace previous work [6, 7], a discrepancy was noticed between the fugacity coefficient of water from the full IAPWS-95 thermodynamic potential and that given by the truncated virial expansion of Feistel et al. [5]. This disagreement is evident even at very low pressures (such as 100 Pa or 1000 Pa) where the truncated virial expansion should be essentially exact. In the rest of this paper, we demonstrate this discrepancy and explain its cause.

2 Analysis

Virial coefficients can be computed from the low-density limits of density derivatives of the IAPWS-95 thermodynamic potential. Wagner and Pruß [2] give expressions relating $B(T)$ to the zero-density limit of ϕ_δ^r and $C(T)$ to the zero-density limit of $\phi_{\delta\delta}^r$, where each subscript δ indicates differentiation with respect to the reduced density δ at constant reduced reciprocal temperature τ .

$$B\rho_c = \lim_{\delta \rightarrow 0} \phi_\delta^r; \quad C\rho_c^2 = \lim_{\delta \rightarrow 0} \phi_{\delta\delta}^r. \quad (4)$$

The fourth virial coefficient $D(T)$ is similarly given by

$$2D\rho_c^3 = \lim_{\delta \rightarrow 0} \phi_{\delta\delta\delta}^r. \quad (5)$$

The derivatives ϕ_δ^r , $\phi_{\delta\delta}^r$, and $\phi_{\delta\delta\delta}^r$ are all available from the Fortran code in the database of Harvey and Lemmon [8], so it was a simple matter to use the code to compute B , C , and D by evaluating the derivatives at very low density ($\delta = 10^{-14}$, verified to be sufficiently close to zero by observing that the derivatives did not change when δ was increased or decreased by an order of magnitude). The results for B and C confirm the values calculated from the expressions of Feistel et al. [5]

The behavior of $D(T)$ from IAPWS-95 has not previously been examined to our knowledge. $D(T)$ reaches extremely large negative values at temperatures below approximately 300 K. This is illustrated in Fig. 1, where we plot (on a logarithmic scale) the magnitudes of C and D normalized and made dimensionless by the second virial coefficient B :

$$C^* = \left| \frac{C}{B^2} \right|; \quad D^* = \left| \frac{D}{B^3} \right|. \quad (6)$$

To illustrate the abnormal behavior of $D^*(T)$ from IAPWS-95, Fig. 1 also includes C^* and D^* derived from the virial coefficients calculated by Benjamin et al. [9] from the TIP4P molecular model of water. While TIP4P would not be expected to quantitatively match the virial coefficients of real water (because it has a liquid-like dipole moment that is too large to represent molecules in the vapor, and also because it ignores multibody forces), it should display the correct qualitative behavior. The normalization by B should also mitigate the effect of the too-large dipole on the higher coefficients.

In Fig. 1, the behavior of $C^*(T)$ from IAPWS-95 is similar to what is expected, although some divergence from the molecular results is seen at the lowest temperatures. For D^* , however, the divergence is much greater, with a difference already roughly two orders of magnitude at 300 K and increasing strongly at lower temperatures.

In principle, this extreme low-temperature behavior of $D(T)$ might not be significant. At low temperatures, vapors only exist at low pressures (low densities), meaning that higher-order terms in the virial expansion might contribute only negligibly even if the virial coefficients are large. To examine this, we consider the effect of the virial terms on the deviation from

ideal-gas behavior. For the fugacity coefficient, the nonideality is simply $\phi - 1$, which can be computed from Eq. (2) for the virial expansion at varying orders of truncation and also from the full IAPWS-95 thermodynamic potential. For computing ϕ from the full IAPWS-95 potential, we use the relationship [4]

$$RT \ln \phi = \mu^r = g^r, \quad (7)$$

where μ^r is the residual chemical potential which for a pure component is equal to the residual molar Gibbs energy g^r . g^r is obtained from ϕ and ϕ_g^r as shown in [2, 3].

Figure 2 shows the fraction of the full IAPWS-95 nonideality recovered by the virial expansion truncated at the second, third, and fourth orders for water at saturated vapor conditions (in equilibrium with ice at and below 273.16 K and with liquid water at and above that temperature). The fraction of the nonideality recovered is defined as $\frac{(\phi - 1)_{\text{vir}}}{(\phi - 1)_{95}}$, the ratio of $(\phi - 1)$ calculated by the virial expansion truncated at a given level with Eq. (2) to that calculated from the full IAPWS-95 potential with Eq. (7). It should be noted that the pressure increases with temperature by several orders of magnitude along the horizontal axis of Fig. 2 according to the vapor-pressure curve $p^{\text{sat}}(T)$, which is obtained from IAPWS-95 for vapor-liquid saturation and from the correlation of Wagner et al. [10] for vapor-solid saturation. This means that the magnitude of $(\phi - 1)$ increases similarly along the horizontal axis.

The high-temperature side of Fig. 2 is physically reasonable. At moderate pressures ($p^{\text{sat}}(500 \text{ K}) \approx 2.6 \text{ MPa}$), the B term recovers most of the nonideality, and the C term recovers most of the remainder. Below about 360 K, however, something strange happens. Even though the pressure is low ($p^{\text{sat}}(350 \text{ K}) \approx 0.04 \text{ MPa}$), the expansion truncated after C is no longer adequate to recover all of the nonideality. The contribution from D becomes larger than that from C , and is necessary to quantitatively recover the nonideality even at conditions of very low pressure ($p^{\text{sat}}(260 \text{ K}) \approx 0.0002 \text{ MPa}$). Table 1 shows the trends in Fig. 2 in tabular form, along with the corresponding pressures and nonidealities. Physically, this behavior would imply that there is a region where four-body collisions affect the thermodynamics much more than three-body collisions despite being much less numerous; this is highly implausible.

To emphasize the abnormality of the behavior shown in Fig. 2, Fig. 3 shows a similar plot made from the recently developed reference equation of state for heavy water [11]. The heavy water formulation behaves as physically expected, with $D(T)$ only contributing at conditions where the saturation pressure is larger.

The same analysis was performed on isobars for pressures of 100 Pa, 1 kPa, 10 kPa, and 100 kPa. Tables 2–5 give a selection of points from the results, which are also plotted for 1 kPa and 100 kPa in Figs. 4 and 5, respectively. Note that a lower temperature limit is set by the saturation temperature for each pressure, since the equilibrium phase at lower temperatures would be a liquid (although the behavior continues smoothly if calculations are extrapolated to the metastable vapor at lower T , and Figs. 4 and 5 extend into that region by 1 or 2 K). At

100 Pa, 1 kPa, and 10 kPa, there is a range of temperatures where the $B+C$ truncation misses a significant part of the nonideality. This is less evident at higher pressures such as 100 kPa, in large part because the vapor part of those isobars does not extend to the low temperatures where D becomes large.

Finally, we note that similar calculations can be performed for other properties that show deviation from ideal-gas behavior, such as the compressibility factor Z . The behavior of Z in this respect is very similar to that of the fugacity coefficient, as would be expected from the similarity between Eqs. (1) and (2).

3 Discussion and Conclusions

The results of the previous section show that, for water vapor between temperatures of approximately 200 K and 350 K, a virial expansion truncated after the B and C terms will omit on the order of 1 % of the derivation from ideal-gas behavior, despite the fact that the virial expansion should converge quickly at these conditions. The maximum fractional effect is approximately 2 %, for the saturated vapor near 268 K.

It should be noted, however, that the problem is not as serious as Figs. 2 and 4 might make it appear. Because the aberrant behavior occurs only at low temperatures (and therefore low vapor pressures and densities), the total nonideality is relatively small. If the nonideality in the vapor-phase fugacity coefficient ($\phi - 1$) is, for example, on the order of 10^{-4} , a 2 % error in a truncated virial expansion leaves the fugacity itself in error by only 2 parts in 10^6 . The largest absolute deviation in the fugacity coefficient due to the unphysical values of D occurs for the saturated vapor near 300 K, where the deviation is approximately 1.4×10^{-5} , or 14 parts in 10^6 . This is small enough that it should be negligible except for precise metrological work.

Because this anomaly has such a small effect on properties of interest such as fugacity or compressibility factor, most scientists or engineers who need water property calculations can continue to use IAPWS-95 without worry. However, caution is necessary for anyone making detailed quantitative calculations of vapor nonideality and virial coefficients in the low-temperature region, because at some conditions virial approximations to IAPWS-95 properties will not converge as they would be expected to at low density.

Even after this analysis, it is not possible to specify the “best” values for the nonideality of low-temperature water vapor. Because experimental data suitable for determining water’s virial coefficients are lacking at low temperatures [12], both IAPWS-95 and any representation of virial coefficients are extrapolations in this region, although both $B(T)$ and $C(T)$ from IAPWS-95 (unlike $D(T)$) extrapolate in a physically reasonable manner. Since the density dependence of low-temperature IAPWS-95 fugacities is wrong at the level of $D(T)$ (in other words, the $D(T)\rho^3$ term in the virial expansion of properties behaves unphysically), it might be preferable to simply use the virial expansion truncated after the $C(T)$ term. While there is currently no way to know whether this would produce more accurate fugacities than the full IAPWS-95 potential, it would at least avoid an unphysical density dependence.

Obtaining more reliable vapor fugacities at these temperatures requires better knowledge of $B(T)$ and $C(T)$ (quantitative knowledge of $D(T)$ should be unnecessary at low vapor densities). Because of the difficulty of measuring water vapor nonideality at low temperatures, the most promising avenue for such improvement is calculation of virial coefficients from high-accuracy *ab initio* intermolecular potentials [13].

We have traced the source of the unphysical low-temperature behavior of $D(T)$ to a single term in the IAPWS-95 formulation. IAPWS-95 includes a sum $\sum_{i=8}^{51} n_i \delta^{d_i} \tau^{t_i} \exp(-\delta^{c_i})$, where δ and τ are the reduced density and reduced reciprocal temperature defined in Section 1. These terms are entirely empirical, and were determined by a structural optimization process [2]. Terms with density exponent $d_i = 3$ contribute to $D(T)$. For the $i = 48$ term, the exponent t_i on τ is 50. This large exponent causes the contribution of this term to $D(T)$ to grow excessively large at low temperatures; this was verified by changing the exponent to a smaller value (10) and observing that the abnormally large values did not occur.

Since the completion of IAPWS-95, developers of reference equations of state have come to recognize that such large exponents are dangerous, especially when extrapolating beyond the range of data used in fitting. More modern formulations take care to avoid large exponents; for example, in the new formulation for heavy water [11] all the t_i are smaller than 6. Taking such precautions with exponents, and paying attention to the behavior of $B(T)$, $C(T)$, and $D(T)$ during fitting, should prevent this problem when developing future equations of state.

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Fig. 1. Normalized third and fourth virial coefficients [Eq. (6)] from IAPWS-95 and from the TIP4P molecular model of water [9]. The curves connecting the TIP4P points are merely guides for the eye

Fig. 2.

Contribution of IAPWS-95 virial terms to nonideality in the fugacity coefficient for the saturated vapor. In Figs. 2–5, the fraction of nonideality recovered is defined as $(\phi - 1)_{\text{vir}} / (\phi - 1)_{95}$, the ratio of $(\phi - 1)$ calculated from the truncated virial expansion to that calculated from the full IAPWS-95 formulation

Fig. 3.

Contribution of virial terms to nonideality in the fugacity coefficient for heavy water according to the equation of state of Herrig et al. [11]

Fig. 4.
Contribution of IAPWS-95 virial terms to nonideality in the fugacity coefficient for the vapor along the 1 kPa isobar

Fig. 5.
Contribution of IAPWS-95 virial terms to nonideality in the fugacity coefficient for the vapor along the 100 kPa isobar

Table 1.

Contribution of virial expansion truncated after B , C , and D to the nonideality in fugacity ($\phi - 1$) for saturated vapor in equilibrium with ice (below 273.16 K) and liquid water (above 273.16 K).

T (K)	p^{sat} (Pa)	$\phi - 1$	$(\phi - 1)_{\text{vir}}/(\phi - 1)_{95}$		
			B	$B+C$	$B+C+D$
180	0.0054	-1.662×10^{-7}	0.9998	0.9998	1.0000
190	0.0324	-5.580×10^{-7}	0.9994	0.9994	1.0000
200	0.1626	-1.824×10^{-6}	0.9984	0.9984	1.0000
210	0.7017	-5.065×10^{-6}	0.9966	0.9966	1.0000
220	2.654	-1.279×10^{-5}	0.9938	0.9938	1.0000
230	8.947	-2.977×10^{-5}	0.9902	0.9903	1.0000
240	27.27	-6.452×10^{-5}	0.9866	0.9867	1.0000
250	76.01	-1.313×10^{-4}	0.9835	0.9837	1.0000
260	195.8	-2.529×10^{-4}	0.9815	0.9819	1.0000
270	470.1	-4.634×10^{-4}	0.9807	0.9815	1.0000
280	991.8	-7.593×10^{-4}	0.9832	0.9846	1.0000
290	1920.	-1.162×10^{-3}	0.9864	0.9886	1.0000
300	3537.	-1.721×10^{-3}	0.9887	0.9920	1.0000
310	6231.	-2.479×10^{-3}	0.9899	0.9946	1.0000
320	1.055×10^4	-3.841×10^{-3}	0.9899	0.9965	1.0000
330	1.721×10^4	-4.776×10^{-3}	0.9890	0.9978	1.0000
340	2.719×10^4	-6.417×10^{-3}	0.9871	0.9986	0.9999
350	4.168×10^4	-8.456×10^{-3}	0.9845	0.9990	0.9999
360	6.219×10^4	-1.095×10^{-2}	0.9813	0.9992	0.9998
370	9.054×10^4	-1.394×10^{-2}	0.9776	0.9992	0.9998
380	1.289×10^5	-1.748×10^{-2}	0.9734	0.9990	0.9997
390	1.796×10^5	-2.162×10^{-2}	0.9688	0.9987	0.9995
400	2.458×10^5	-2.640×10^{-2}	0.9640	0.9982	0.9994
420	4.373×10^5	-3.796×10^{-2}	0.9537	0.9970	0.9990
440	7.337×10^5	-5.234×10^{-2}	0.9428	0.9953	0.9985
460	1.171×10^6	-6.960×10^{-2}	0.9314	0.9931	0.9979
480	1.790×10^6	-8.966×10^{-2}	0.9198	0.9903	0.9971
500	2.639×10^6	-1.124×10^{-1}	0.9080	0.9867	0.9959

Table 2.

Contribution of virial expansion truncated after B , C , and D to the nonideality in fugacity ($\varphi - 1$) for water vapor at 100 Pa.

T (K)	$\varphi - 1$	$(\varphi - 1)_{\text{vir}}/(\varphi - 1)_{95}$		
		B	$B+C$	$B+C+D$
253	-1.579×10^{-4}	0.9834	0.9836	1.0000
260	-1.274×10^{-4}	0.9950	0.9952	1.0000
270	-9.681×10^{-5}	0.9991	0.9991	1.0000
280	-7.532×10^{-5}	0.9997	0.9998	1.0000
290	-5.972×10^{-5}	0.9999	1.0000	1.0000
300	-4.817×10^{-5}	0.9999	1.0000	1.0000
320	-3.274×10^{-5}	0.9999	1.0000	1.0000
350	-2.006×10^{-5}	1.0000	1.0000	1.0000
400	-1.049×10^{-5}	1.0000	1.0000	1.0000
500	-4.079×10^{-6}	1.0000	1.0000	1.0000

Table 3.

Contribution of virial expansion truncated after B , C , and D to the nonideality in fugacity ($\phi - 1$) for water vapor at 1 kPa.

T (K)	$\phi - 1$	$(\phi - 1)_{\text{vir}}/(\phi - 1)_{95}$		
		B	$B+C$	$B+C+D$
281	-7.458×10^{-4}	0.9853	0.9867	1.0000
290	-5.996×10^{-4}	0.9957	0.9969	1.0000
300	-4.823×10^{-4}	0.9984	0.9994	1.0000
310	-3.946×10^{-4}	0.9991	0.9999	1.0000
320	-3.275×10^{-4}	0.9993	1.0000	1.0000
340	-2.338×10^{-4}	0.9996	1.0000	1.0000
360	-1.737×10^{-4}	0.9997	1.0000	1.0000
380	-1.332×10^{-4}	0.9998	1.0000	1.0000
400	-1.049×10^{-4}	0.9999	1.0000	1.0000
500	-4.079×10^{-5}	1.0000	1.0000	1.0000

Table 4.

Contribution of virial expansion truncated after B , C , and D to the nonideality in fugacity ($\phi - 1$) for water vapor at 10 kPa.

T (K)	$\phi - 1$	$(\phi - 1)_{\text{vir}}/(\phi - 1)_{95}$		
		B	$B+C$	$B+C+D$
319	-3.425×10^{-3}	0.9900	0.9964	1.0000
320	-3.299×10^{-3}	0.9906	0.9969	1.0000
330	-2.763×10^{-3}	0.9941	0.9993	1.0000
340	-2.345×10^{-3}	0.9956	0.9998	1.0000
350	-2.011×10^{-3}	0.9964	0.9999	1.0000
360	-1.740×10^{-3}	0.9970	1.0000	1.0000
380	-1.334×10^{-3}	0.9979	1.0000	1.0000
400	-1.050×10^{-3}	0.9985	1.0000	1.0000
500	-4.080×10^{-4}	0.9997	1.0000	1.0000

Table 5.

Contribution of virial expansion truncated after B , C , and D to the nonideality in fugacity ($\phi - 1$) for water vapor at 100 kPa.

T (K)	$\phi - 1$	$(\phi - 1)_{\text{vir}}/(\phi - 1)_{95}$		
		B	$B+C$	$B+C+D$
373	-1.481×10^{-2}	0.9766	0.9991	0.9997
380	-1.351×10^{-2}	0.9795	0.9995	0.9999
390	-1.192×10^{-2}	0.9828	0.9997	1.0000
400	-1.059×10^{-2}	0.9855	0.9998	1.0000
450	-6.296×10^{-3}	0.9933	0.9999	1.0000
500	-4.085×10^{-3}	0.9965	1.0000	1.0000