On the suitability of the virial equation for modeling the solubility of solids in supercritical fluids

Allan H. Harvey

Physical and Chemical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, CO 80303, USA

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Abstract

Five model systems, the van der Waals fluid, the Soave–Redlich–Kwong fluid, the Peng–Robinson fluid, the hard-sphere fluid, and the square-well fluid, are used to examine the performance of the truncated virial expansion in describing the fugacity of a solute at infinite dilution in a solvent. It is demonstrated that the virial fugacity results deteriorate at significantly lower densities as the solute becomes larger. This has consequences for attempts to describe the solubility of solids in supercritical fluids, where the virial expansion, truncated after the third virial coefficient, has been considered as a modeling option. The results of this work suggest that, for the densities and solute-to-solvent size ratios commonly encountered in supercritical extraction, the truncated virial expansion should not be expected to describe correctly the solute fugacity, and therefore any success it has in fitting solubility data should be viewed with caution. © 1997 Elsevier Science B.V.

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1. Introduction

There continues to be substantial interest in separation technology utilizing supercritical fluids (Bruno and Ely, 1991). Since phase equilibrium is fundamental to most such processes, there is a need for effective models to describe the equilibrium between a condensed phase and a supercritical fluid phase. The large asymmetries (particularly in molecular size, but often also in polarity and other structure-related properties) between the extracting fluid and the substance being extracted makes this modeling more challenging than that for traditional systems such as hydrocarbon mixtures.
The modeling becomes simpler if the condensed phase is a solid. In that case, the solid can usually be assumed to be pure (with a fugacity given by the product of its vapor pressure and a Poynting correction), and the only non-ideality is that in the supercritical fluid phase. Often the solute is sufficiently involatile that it can be considered infinitely dilute in the fluid phase, further simplifying matters. Most models of such systems have been based on equations of state for the supercritical fluid mixture or on semi-empirical correlations with density as the independent variable. These efforts were reviewed by Johnston et al. (1989); more recent work includes that of Harvey (1990), Mukhopadhyay and Rao (1993), Kwon and Mansoori (1993), and Wang and Tavlarides (1994).

Another possible method for modeling these systems is to describe the fluid phase with the virial equation of state. Second virial coefficients were first used in this way by Perkins (1937). This approach was used extensively by Robin (1951) and Robin and Vodar (1953). Ewald et al. (1953) extended the method to the level of the third virial coefficient. The virial expansion to the third virial coefficient has recently been used by Quiram et al. (1994) to produce a linear correlating equation for the solubility of solid solutes in supercritical fluids.

The fairly good fit to data by Quiram et al. (1994) was surprising (as they noted), since the data often extended to densities more than twice the solvent’s critical density. It is known that, for describing the PVT behavior of pure fluids, results from the virial expansion truncated after the third coefficient begin to deteriorate at about half the critical density and are poor by the time the critical density is reached. If the same holds true for the fugacity of a solute in a supercritical solvent, then any fit to solubility data much beyond half the solvent’s critical density with such a method must be attributed to factors other than the theoretical basis of the model. One might even expect the results to be worse for the typical situation of large solutes in a smaller solvent, since the omitted higher-order virial coefficients describing the interaction between a single solute molecule and multiple solvent molecules would be expected to be larger than for mixtures of equal-sized molecules.

It is difficult to test this hypothesis with experimental data, since few systems have precise data measured over a range from very low solvent densities, where the truncated virial expansion should be accurate, to high densities where it could be expected to fail. Chueh and Prausnitz (1967) report that their description of the solubility of solid methane in hydrogen with a third virial coefficient fit to the data works only to about hydrogen’s critical density; similar behavior can be seen in the description by Ewald et al. (1953) of the solubility of solid carbon dioxide in air. Neither of these mixtures, however, has the large molecular size difference characteristic of most supercritical extraction systems.

In this work, we use model fluids, for which exact results can be obtained at any density, to compare with results of the truncated virial expansion. Two questions are of interest for solutes dilute in a supercritical solvent: (1) at what density does the truncated virial expansion cease to describe adequately the solute fugacity; (2) what is the effect of the solute-to-solvent size ratio on the answer to (1). We use five models to analyze these issues for systems chosen to mimic those commonly encountered in supercritical fluid extraction.

2. Analysis for van der Waals fluid

We first consider a hypothetical fluid whose behavior is exactly described by the van der Waals equation of state with simple Lorentz–Berthelot combining rules. For a mixture with the solute
(species 2) infinitely dilute in solvent (species 1), the solute fugacity coefficient $\phi_2$ is given by (Prausnitz et al., 1986)

$$\ln \phi_2 = \ln \left( \frac{v}{v - b_1} \right) + \frac{b_2}{v - b_1} - \frac{2\sqrt{a_1a_2}}{vRT} - \ln z$$

(1)

where $a$ and $b$ are the van der Waals energy and volume parameters, $v$ is the molar volume, and $z$ is the compressibility factor $Pv/RT$.

We can also compute the second and third virial coefficients from the van der Waals equation. For solute fugacity computations at infinite dilution, the relevant coefficients are those involving one solute molecule ($B_{12}$ and $C_{112}$). These are

$$B_{12} = 0.5(b_1 + b_2) - \frac{\sqrt{a_1a_2}}{RT}$$

(2a)

$$C_{112} = \frac{1}{3}(2b_1b_2 + b_1^2)$$

(2b)

The fugacity coefficient in the truncated virial expansion is calculated from (Prausnitz et al., 1986)

$$\ln \phi_{2v} = \frac{2}{v}B_{12} + \frac{3}{2v^2}C_{112} - \ln z$$

(3)

where the superscript $v$ indicates that the fugacity coefficient has been calculated according to the truncated virial expansion. The compressibility factor $z$ in Eq. (3) could in principle be calculated from the truncated virial expansion. However, it is possible for $z$ calculated in that manner to become negative (this happens at a reduced density near 1.2 on the critical isotherm of the van der Waals fluid). The alternative, since the behavior of the pure solvent is typically well known, is to use the exact value of $z$. This is the approach generally taken in virial-equation analyses of supercritical solubility, and it is the one we use throughout this work.

We now examine how well the truncated virial expansion reproduces the exact fugacity coefficient as computed by the equation of state. For the solvent, we choose a hypothetical van der Waals fluid with the same critical parameters as carbon dioxide. For solutes, we choose benzene, naphthalene, and anthracene to examine a variety of size ratios. Critical parameters were taken from a DIPPR (1994) compilation.

Fig. 1 shows, for a temperature equal to the solvent’s critical temperature, the ratio of the fugacity coefficient derived from the truncated virial equation to the exact value as a function of the solvent’s reduced density $\rho/\rho_c$, where $\rho_c$ is the critical density. In addition to the ratio for the three solutes, that for the solvent (or a solute identical with the solvent) is also plotted. It is clear that, by the time $\rho_c$ is reached, the virial fugacity is only a fair approximation to the exact fugacity for a solute identical with the solvent. For larger solutes, the error becomes significant at lower densities and is severe at and above the critical density.

3. Analysis for Soave–Redlich–Kwong fluid

The van der Waals equation is only qualitatively correct for real fluids; we now turn to more accurate equations of state commonly used in engineering practice. We first consider a fluid whose
behavior is exactly described by the Soave (1972) modification of the Redlich–Kwong equation of state (hereafter referred to as SRK). For the SRK equation, the solute fugacity coefficient \( \phi_2 \) at infinite dilution is given by (Prausnitz et al., 1986)

\[
\ln \phi_2 = \ln \left( \frac{v}{v - b_1} \right) + \frac{b_2}{v - b_1} - \frac{2\sqrt{a_1 a_2}}{R T b_1} \ln \left( \frac{v + b_1}{v} \right) - \ln z \\
+ \frac{a_1 b_2}{R T b_1^2} \left( \ln \left( \frac{v + b_1}{v} \right) - \frac{b_1}{v + b_1} \right)
\]

(4)

where \( a \) and \( b \) are the SRK energy and volume parameters.

The relevant second and third virial coefficients derived from the SRK equation are

\[
B_{12} = 0.5 \left( b_1 + b_2 \right) - \frac{\sqrt{a_1 a_2}}{R T} \quad (5a)
\]

\[
C_{112} = \frac{1}{3} \left( 2b_1 b_2 + b_1^2 \right) + \frac{1}{3RT} \left( 2\sqrt{a_1 a_2} b_1 + a_1 b_2 \right) \quad (5b)
\]

We perform the same calculations for the SRK fluid as for the van der Waals fluid. The results are shown in Fig. 2. Again, the truncated virial equation becomes inadequate for computing the fugacity.
at intermediate densities, and the error is larger for larger solutes. It is interesting that the truncated virial equation overestimates the solute fugacity coefficients, whereas it underestimated them for the van der Waals equation. The cause is probably the different way in which the attractive term of each equation contributes to the virial coefficients. For the van der Waals fluid, the attractive term does not contribute to any virial coefficients beyond the second. For the SRK fluid, the attractive term makes a negative contribution to the second virial coefficient, a positive contribution to the third, a negative contribution to the fourth, and so on. This results in a much more positive third virial coefficient for the SRK fluid, leading to the result shown in Fig. 2.

4. Analysis for Peng–Robinson fluid

The other widely used cubic equation of state is that developed by Peng and Robinson (1976). The solute fugacity coefficient $\phi_2$ at infinite dilution is given by (Prausnitz et al., 1986)

$$
\ln \phi_2 = \frac{b_2}{b_1} (z - 1) - \ln \left( \frac{P (v - b_1)}{RT} \right) - \frac{a_1}{2 \sqrt{2} b_1 RT} \left( \frac{2 \sqrt{a_1 a_2}}{a_1} - \frac{b_2}{b_1} \right) \ln \left( \frac{v + (1 + \sqrt{2}) b_1}{v + (1 - \sqrt{2}) b_1} \right)
$$

(6)

where $a$ and $b$ are the Peng–Robinson energy and volume parameters.
The relevant second and third virial coefficients are

\[ B_{12} = 0.5(b_1 + b_2) - \frac{\sqrt{a_1a_2}}{RT} \]  
(7a)

\[ C_{112} = \frac{1}{3} \left( 2b_1b_2 + b_1^2 \right) + \frac{2}{3RT} \left( 2\sqrt{a_1a_2}b_1 + a_1b_2 \right) \]  
(7b)

We perform the same calculations as before; the Peng–Robinson results are similar to those shown in Fig. 2 except that the deviations of the fugacity coefficient ratio from unity are several times larger than for the SRK equation. This is probably again attributable to the virial expansions of the equations of state; the contributions of the attractive term to the higher virial coefficients for the Peng–Robinson equation are larger than for the SRK (twice as large in the case of the third virial coefficient). The variance in behavior between three cubic equations of state suggests that some other cubic form with a third virial coefficient intermediate between that from the van der Waals and SRK equations might produce a truncated virial expansion that was better behaved with respect to the full equation of state.

5. Analysis for hard-sphere fluid

It is interesting to see whether the effects observed for cubic equations of state occur in a simple model with only repulsive forces. A tractable model is a mixture of hard spheres, for which the fluid properties are given to good accuracy by the equation of Boublik (1970) and Mansoori et al. (1971). Equations for calculating fugacity coefficients from the Boublik–Mansoori equation were taken from Dimitrelis and Prausnitz (1986).

The relevant second and third virial coefficients in a binary mixture of hard spheres with diameters \( \sigma_1 \) and \( \sigma_2 \) are given by Mason and Spurling (1969):

\[ B_{12} = \frac{2\pi}{3} N_A \sigma_{12}^3 \]  
(8a)

\[ C_{112} = \left( \frac{2\pi N_A}{3} \right)^{2} \left( \frac{1}{24} \right) \left( \sigma_1^6 - 18\sigma_1^4\sigma_{12}^2 + 32\sigma_1^3\sigma_{12}^3 \right) \]  
(8b)

where the unlike diameter \( \sigma_{12} = 0.5(\sigma_1 + \sigma_2) \) and \( N_A \) is Avogadro’s number. To simplify the analysis, we take \( \sigma_1 \) as the unit length and work in terms of a reduced density \( \rho^* = \rho N_A \sigma_1^3 \). Then reduced virial coefficients are defined by removing the factors of \( N_A \) from Eqs. (8a) and (8b) and setting \( \sigma_1 \) to unity. Eq. (3) can then be used for the fugacity with these reduced virials and with the volume replaced by the reciprocal of the reduced density.

Fig. 3 shows, as a function of \( \rho^* \), the ratio of the truncated virial fugacity coefficient to the value from the Boublik–Mansoori equation. The ratio is plotted for five values of the solute-to-solvent diameter ratio ranging from 1 to 2. For comparison with Figs. 1 and 2, a rough estimate (based on the cube roots of the critical volumes) of diameter ratios with carbon dioxide as the solvent yields ratios of 1.40 for benzene, 1.64 for naphthalene, and 1.81 for anthracene. While there is no critical point for
the hard-sphere fluid, a value of $\rho^* = 0.35$ roughly corresponds to the critical density of simple fluids.

As with the other fluids, the solute fugacity coefficient deviates farther from the exact value at a given reduced density as the size ratio increases. This shows that even when only excluded volume effects are considered, the truncated virial expansion is limited in its ability to describe solute fugacities, especially for large solutes.

6. Analysis for square-well fluid

Finally, we examine an exact potential model with both repulsive and attractive forces. The square-well fluid is the most realistic model for which mixture second and third virial coefficients are known analytically. The 'exact' fugacity of a solute in a square-well mixture can be calculated by computer simulation.

For the square-well fluid, the intermolecular potential $U_{ij}(r_{ij})$ is defined as follows:

$$
U_{ij}(r_{ij}) = \begin{cases} 
\infty & (r_{ij} < \sigma_{ij}) \\
-\epsilon_{ij} & (\sigma_{ij} \leq r_{ij} < \lambda_{ij}\sigma_{ij}) \\
0 & (r_{ij} \geq \lambda_{ij}\sigma_{ij})
\end{cases}
$$

(9)
For unlike-pair interactions, the combining rules for $\sigma_{ij}$ and $\lambda_{ij}$ are

$$\sigma_{ij} = 0.5(\sigma_i + \sigma_j) \quad (10a)$$
$$\lambda_{ij} = 0.5(\lambda_i + \lambda_j) \quad (10b)$$

For the well depth $\epsilon_{ij}$, we choose the customary geometric mean combining rule:

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2} \quad (10c)$$

The second virial coefficient for this potential is (Hirschfelder et al. (1954)):

$$B_{ij} = \frac{2\pi}{3} N_A \sigma_{ij}^3 \left[ 1 - \left( \lambda_{ij}^3 - 1 \right) \Delta_{ij} \right] \quad (11)$$

where $\Delta_{ij} = [\exp(\epsilon_{ij}/kT) - 1]$. The expressions for the third virial coefficients of square-well fluid mixtures are lengthy; see Hirschfelder et al. (1954) and Kihara (1955).

Exact values of the fugacity coefficients in square-well mixtures were calculated in Monte Carlo computer simulations. The fugacity coefficient $\phi_i$ for a solute species $i$ is related to the residual chemical potential, which may be calculated by the test-particle insertion method (Widom, 1963; Jackson and Klein, 1964). The expression in the NVT ensemble is

$$\phi_i z = \exp\left(-\frac{U_i}{kT}\right)^{-1} \quad (12)$$

where $\langle \exp(-U_i/kT) \rangle$ is an expectation value computed by sampling the interaction energies $U_i$ of a hypothetical test particle throughout the simulation cell. The compressibility factor is computed from the virial of the forces; for the square-well fluid it is given by

$$z = 1 + \frac{2\pi}{3} \rho \sigma^3 \left[ g(\sigma^+) - \lambda^3 \left( g(\lambda \sigma^-) - g(\lambda \sigma^+) \right) \right] \quad (13)$$

where $g$ is the radial distribution function (accumulated during the simulation) and the plus and minus superscripts indicate limits as the discontinuity in the potential is approached from above and below.

All comparisons were performed with the range parameter $\lambda$ at 1.5. For this well-width, the reduced critical temperature $T_c^* = kT_c/\epsilon$ is found to be approximately 1.22 by Gibbs ensemble simulation (Vega et al., 1992). The simulations and virial calculations in this work were therefore performed at a reduced temperature $kT/\epsilon$ of 1.3 to ensure that they corresponded to a supercritical isotherm.

Simulations were performed in the NVT ensemble using 300 solvent particles with periodic boundary conditions. After equilibration at each density, a total of 60–100 million trial particle moves were attempted. The maximum magnitude of a move was chosen so that approximately half the attempted moves would be accepted.

To evaluate solute fugacity coefficients using Eq. (12), 1000 ‘solute’ sites were placed on a cubic lattice in the simulation cell. The test particle insertion method is non-intrusive, so any number of solute particles can be examined simultaneously. Solute were examined with diameters (relative to $\sigma_1$) of 1.0, 1.25, 1.5, 1.75, and 2.0. To mimic real fluids, larger solutes should also have a somewhat deeper potential well; we arbitrarily chose to set $\epsilon_2/\epsilon_1 = \sigma_2/\sigma_1$ for each solute. Fugacity coeffi-
Table 1
Simulation results for solutes at infinite dilution in a square-well fluid with $\lambda = 1.5$ and $T^* = 1.3$

<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>z</th>
<th>$(\phi_2 z)_{1.0}$</th>
<th>$(\phi_2 z)_{1.25}$</th>
<th>$(\phi_2 z)_{1.5}$</th>
<th>$(\phi_2 z)_{1.75}$</th>
<th>$(\phi_2 z)_{2.0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>0.913</td>
<td>0.8360(4)</td>
<td>0.7211(3)</td>
<td>0.5787(4)</td>
<td>0.4234(7)</td>
<td>0.2756(7)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.824</td>
<td>0.7050(4)</td>
<td>0.5277(6)</td>
<td>0.3425(6)</td>
<td>0.1844(10)</td>
<td>0.0783(11)</td>
</tr>
<tr>
<td>0.10</td>
<td>0.679</td>
<td>0.5167(4)</td>
<td>0.2981(13)</td>
<td>0.1309(9)</td>
<td>0.0404(7)</td>
<td>0.0081(8)</td>
</tr>
<tr>
<td>0.15</td>
<td>0.572</td>
<td>0.3951(5)</td>
<td>0.1827(9)</td>
<td>0.0579(5)</td>
<td>0.0112(5)</td>
<td>0.0011(6)</td>
</tr>
<tr>
<td>0.20</td>
<td>0.484</td>
<td>0.3143(9)</td>
<td>0.1208(7)</td>
<td>0.0296(4)</td>
<td>0.00394(29)</td>
<td>0.00027(3)</td>
</tr>
<tr>
<td>0.25</td>
<td>0.418</td>
<td>0.2591(10)</td>
<td>0.0855(8)</td>
<td>0.0168(6)</td>
<td>0.00176(12)</td>
<td>--</td>
</tr>
<tr>
<td>0.30</td>
<td>0.354</td>
<td>0.2197(8)</td>
<td>0.0644(4)</td>
<td>0.0106(4)</td>
<td>0.00090(14)</td>
<td>--</td>
</tr>
<tr>
<td>0.35</td>
<td>0.329</td>
<td>0.1916(9)</td>
<td>0.0504(5)</td>
<td>0.00749(15)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.40</td>
<td>0.323</td>
<td>0.1718(13)</td>
<td>0.0412(5)</td>
<td>0.00532(21)</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

cients (as the product $\phi_2 z$ given by Eq. (12)) were evaluated at nine different reduced densities (where the reduced density is again defined by $\rho^* = \rho N_A \sigma_i^3$) from 0.025 to 0.4.

The results are given in Table 1. The subscripts on the $\phi_2 z$ column headings represent the values of $\epsilon_2/\epsilon_1 = \sigma_2/\sigma_1$ for that solute. The numbers in parentheses represent the standard deviation in the last digit; these were estimated in the customary manner by dividing the simulation run into ten blocks and taking the standard deviation. For the largest solutes at the highest densities, the simulation runs

Fig. 4. Ratio of truncated virial fugacity coefficients to exact values for solutes of various diameter and well-depth ratios in a square-well fluid on a supercritical isotherm.
were not long enough to obtain a reliable result; these entries in the table are left blank. No formal estimate was made of the uncertainty in the compressibility factor \( z \), but the radial distribution functions are sufficiently well established by the simulation that the reported values should be accurate to about \( \pm 1 \) in the last digit.

In Fig. 4, the ratio of the truncated virial fugacity coefficient to that from the simulations is plotted for each solute. The error bars correspond to the standard deviations in Table 1; points are shown without error bars if the uncertainty is less than the size of the symbol. The lines in Fig. 4 simply connect the different points for each value of the size ratio. Similar to the other systems, the fugacity coefficient of a solvent-sized solute is described adequately up to perhaps the critical density (about \( \rho^* = 0.3 \) (Vega et al., 1992), but for larger solutes the truncated virial fugacity becomes unacceptable at substantially lower densities.

7. Discussion and conclusions

Supercritical extraction most often involves relatively large solutes in a solvent made of smaller molecules. Physical intuition suggests that a virial description of a solute's fugacity would be worse for a larger solute, because it would be interacting with more solvent molecules even at relatively low densities. The examples in this work confirm this intuition. The truncated virial expansion does not
yield good results for these systems at densities near and above the solvent’s critical density. This is, however, exactly the density regime in which data exist for most systems; also, the high-pressure side of a supercritical extraction process would operate at densities perhaps twice the critical density. At a fundamental level, then, one cannot endorse the use of virial-based correlation methods for supercritical extraction systems.

There is still a puzzle with regard to the work of Quiram et al. (1994), who found that their truncated virial model fitted experimental data better than this analysis suggests that it should have. Some insight may be obtained from Figs. 5 and 6, in which Quiram’s combination of variables \(\ln(z\phi_2)/\rho\) (with \(\rho\) replaced by the reduced density \(\rho/\rho_c\)) is plotted vs. reduced density for SRK and Peng–Robinson fluid mixtures with parameters chosen to correspond to naphthalene in carbon dioxide at the critical temperature of CO\(_2\). The solid curves represent the exact behavior of the equation of state, while the dashed lines are the predictions of the truncated virial expansion. As seen in Fig. 2, the virial and the exact results part company at low densities. In both cases, however, the two results cross each other at high densities (this means that if Fig. 2 were drawn to much higher densities, the curves would reach a maximum and then decline, eventually crossing to values below unity).

The interesting aspect of Figs. 5 and 6 is the large quasi-linear region in each, indicated by the dotted lines. For the SRK fluid, this extends from a reduced density of about 0.4 to perhaps 1.8; for the Peng–Robinson fluid the range is about 0.8 to 2.2. This suggests that, when supercritical solubility

Fig. 6. Quantity \(\ln(z\phi_2)/\rho^*\) as given by the truncated virial expansion and by the full equation for naphthalene in CO\(_2\) at the critical temperature of CO\(_2\), according to the Peng–Robinson equation of state. The dotted line is drawn through the region of approximate linearity.
data are plotted on these coordinates, linear behavior may appear. This is only a tentative explanation because the apparent linearity may be an artifact of the equations of state; the van der Waals fluid does not show such a region when plotted in this manner. But the SRK and Peng–Robinson calculations at least make it plausible that real fluid behavior could produce linearity over a range of densities as shown in Figs. 5 and 6.

It is important to note that the apparent linearity shown in Figs. 5 and 6 will not produce the correct virial coefficients. In Quiram’s formulation, the slope of this line is related to the third cross virial coefficient $C_{112}$, while the intercept is related to the second cross virial coefficient $B_{12}$. At least for the SRK and Peng–Robinson fluids, this will apparently produce a fairly small error for $B_{12}$ but a much larger error for $C_{112}$.

In summary, the truncated virial expansion with the correct virial coefficients is not adequate for describing the fugacity of the solute (and therefore its solubility) at conditions typically encountered in supercritical fluid extraction. For reasons not yet understood, a correlation based on the virial expansion such as that of Quiram et al. (1994) may nevertheless fit experimental data. It should be recognized, however, that such fits are unlikely to yield the true virial coefficients (especially third virial coefficients), and, conversely, that correct values of the virial coefficients are unlikely to yield correct solubilities at moderate and high densities.

After this work was completed, a paper appeared by Joslin et al. (1996) that supports some of the conclusions reached here. They examined mixtures of Lennard-Jones molecules, finding that truncation after the third virial coefficient was inadequate for describing solute chemical potentials near and above the critical density. Including the fourth virial coefficient increased the range of applicability significantly. As found in this work, the performance of the virial equation was worse for larger solute-to-solvent size ratios.

8. List of symbols

$B$ second virial coefficient
$C$ third virial coefficient
$N_A$ Avogadro’s constant
$P$ pressure
$R$ ideal gas constant
$T$ absolute temperature
$U$ intermolecular potential energy
$a, b$ constants in van der Waals, SRK, or Peng–Robinson equation of state
$g$ radial distribution function
$k$ Boltzmann’s constant
$r$ intermolecular distance
$v$ molar volume
$z$ compressibility factor, $Pv/RT$

8.1. Greek Letters

$\Delta$ function of well depth appearing in Eq. (11)
$\epsilon$ well depth for square-well potential
\(\phi\) fugacity coefficient
\(\lambda\) parameter describing width of attractive well
\(\rho\) molar density
\(\sigma\) molecular hard-core diameter

8.2. Subscripts
1 solvent species
2 solute species
c critical value
\(i,j\) arbitrary species

8.3. Superscripts
\(v\) calculated from truncated virial expansion
\(+, -\) limits as intermolecular distance approached from above, below
\(*\) reduced quantity

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