Mayer-sampling Monte Carlo calculations of uniquely flexible contributions to virial coefficients

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We present methods for computing contributions to the virial coefficients uniquely associated with molecular flexibility, and we demonstrate their use with application to the third, fourth, and fifth virial coefficients of united-atom models of linear alkanes and methanol belonging to the suite of transferrable potentials for phase equilibria (TraPPE-UA). We find that these uniquely flexible contributions are more difficult to compute than the remainder of the coefficient, especially for the conditions at which they appear to be most important. The significance of these contributions relative to the full virial coefficient grows with the number of sites (the size of the molecule), the number of molecules, and, to a certain extent, the temperature. The nature of the site-site interactions is of great importance: the significance of the uniquely flexible contribution at third and fourth order is orders of magnitude larger for TraPPE-UA methanol, which has Coulombic interactions, than for TraPPE-UA propane, which does not, even though both models have three sites per molecule and comparable bending potentials. While the uniquely flexible contribution of TraPPE-UA propane has a negligible impact on its third-order virial-equation-of-state estimate of the critical point, the uniquely flexible contribution of TraPPE-UA methanol increases this estimate of its critical pressure by about 5%.


I. INTRODUCTION

The virial equation of state (VEOS) is a powerful tool for examination of molecular models. As presented in Eq. (1), \( P = \frac{n}{kT} \sum B_n \rho^{n-1} \) (1)

Caracciolo et al. showed that these definitions are different for rigid and flexible molecular models, and they have derived the uniquely flexible contributions to \( B_3 \) and \( B_4 \). They applied the expressions within the context of a polymer solution, modeled as a lattice for computational convenience. Here, we present and examine uniquely flexible contributions for off-lattice molecular models within the context of low-density vapors, computed via the Mayer-sampling Monte Carlo (MSMC) method. We further extend the development to include \( B_5 \).

For pairwise-additive models, the virial coefficients \( B_n \) are defined in terms of integrals involving the Mayer function, \( f_{ij} = \exp(-\beta u_{ij}) - 1 \). Within the context of the virial equation of state for dilute gases, \( u_{ij} \) is the interaction energy between molecules \( i \) and \( j \). For osmotic virial coefficients, the context considered by Caracciolo et al., \( u_{ij} \) is the potential of mean force between particles \( i \) and \( j \) within a solvent.

Aside from this difference in \( u_{ij} \), expressions for virial coefficients and osmotic virial coefficients are equivalent. The integrals that give \( B_n \) from the molecular model are often depicted with a diagram notation in which \( f_{ij} \) is drawn as a line between molecules \( i \) and \( j \), represented as points. For homogeneous systems such as a bulk fluid, it is acceptable to consider molecule 1 fixed at the origin. Molecule 1 is represented with a white circle, as can be seen in Eq. (2) for \( B_2 \), and is referred to as a root molecule. The positions of other molecules \( r_j \) are integration variables, and these molecules are represented with black circles.

\[ B_2 = -\frac{1}{2} \int f_{12} \, dr_2 = -\frac{1}{2} \langle f_{12} \rangle \] (2)

The angled brackets in Eq. (2) denote an ensemble average over the coordinates defining orientation \( \omega_j \) and intramolecular degrees of freedom \( c_j \), as shown in Eq. (3). If the molecular model is anisotropic, one must average over \( \omega_j \) in addition to integrating over \( r_j \), which we define using the molecules’ geometric centers. If the molecules have intramolecular degrees of freedom \( c_j \), one must also average over these in proportion to the Boltzmann factors associated with their intramolecular energies \( u_j \):

\[ \langle f_{12} \rangle = \frac{\int f_{12} e^{-\beta u_{12}} dc_1 dc_2 d\omega_1 d\omega_2}{\int e^{-\beta u_{12}} dc_1 dc_2 d\omega_1 d\omega_2} \] (3)

The Caracciolo et al. formulation of \( B_3 \) is shown in Eq. (4). We continue their use of \( I_n \) to refer to the biconnected diagrams of \( B_n \); the diagrams in which at least two independent paths may be drawn connecting any two molecules in
the diagram. The non-biconnected diagrams of $B_n$ are either singly connected or disconnected. As described in Sec. II, it is advantageous to compute sums of singly connected and disconnected diagrams from a common set of configurations, importance sampled on the sum. To combine the singly connected three-molecule chain and disconnected $-I_1^2$ into one integral $T_1$ (Eq. (4b)), one must consider a fourth molecule, which we refer to as molecule 1’. The geometric center of molecule 1’ may be fixed at the origin like molecule 1, but its intramolecular degrees of freedom are independent from those of molecule 1, as can be seen in Eq. (5). We refer to $B_n^{NBC}$ as the uniquely flexible contribution to $B_n$. As presented in Eq. (4b), $B_3^{NBC} = -T_1$ measures the sensitivity of the interaction between molecule 1 and molecule 3 to the intramolecular conformation of molecule 1. Note that the conformations sampled by molecule 1 will differ from those sampled by molecule 1’ because the former interacts with molecule 2, while the latter does not. To the extent that this difference affects interactions with molecule 3, $T_1$ will be nonzero.

$$B_3 = -\frac{1}{3}I_1 - T_1$$

$$I_1 = \int \langle f_{12} f_{13} f_{23} \rangle d\mathbf{r}_2 d\mathbf{r}_3 =$$

$$T_1 = \int \langle f_{12} (f_{13} - f_{13}') \rangle d\mathbf{r}_2 d\mathbf{r}_3 =$$

In $B_4$, there are three singly connected diagrams consisting of all four molecules, which lead to three terms analogous to $T_1$. The Caracciolo et al. formulations of $B_4$ and its $T_i$ terms are shown below in Eq. (6), where we have rewritten $T_i$ to indicate two alternates of molecule 1: 1’ and 1’’. Molecule 1’’ is represented with a hatched circle.

$$B_4 = -\frac{1}{8}I_4 - \frac{1}{2}T_2 - \frac{3}{2}T_3 - \frac{3}{2}T_4 + \frac{9}{2}I_2 T_1$$

$$I_4 = \int \langle f_{12} f_{23} f_{34} f_{14} \rangle (3 + 6 f_{13} + f_{13} f_{24}) d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

$$T_2 = \int \langle f_{12} (f_{13} - f_{13}' f_{24}) \rangle d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

$$T_3 = \int \langle f_{12} (f_{23} f_{34} - f_{13} f_{24}) \rangle d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

The Mayer-sampling Monte Carlo method used to compute the uniquely flexible contributions for TraPPE-UA alkanes, as well as the modifications to the approach required for TraPPE-UA methanol because of its Coulombic interactions. We present our results in Sec. III, where we analyze the significance of the uniquely flexible contribution to the virial coefficients and VEOS estimates of the critical point. For TraPPE-UA methanol, we also examine the impact of the
extension of the oxygen–hydrogen bond that resulted from rounding the bond length. We conclude in Sec. IV.

II. METHODS

We employ the overlap-sampling formulation of Maysampling Monte Carlo, described in detail in Ref. 5, to compute \( B_n \) and portions thereof. The method employs a hypothetical overlap system having integrands intermediate between that of the target integral, evaluated with a TraPPE-UA potential, and that of the reference integral, evaluated with a hard-sphere potential. Each molecule in the reference is a single hard sphere, regardless of the number of atoms in the target potential. To compute the biconnected contributions \( B_n^{BC} \), we employ the corresponding hard-sphere virial coefficient as the reference integral. To compute the non-biconnected contributions \( B_n^{NBC} \), we employ the singly connected diagrams evaluated for hard spheres as the reference integral for up to fifth order, and, at fifth order, we employ \( B_5 \) for hard spheres as the reference integral. The calculation is not particularly sensitive to the choice of the hard-sphere diameter, and we employ the same hard-sphere diameters used previously for the biconnected contributions: 5 Å for TraPPE-UA methanol, 5.25 Å for TraPPE-UA propane, 5.75 Å for TraPPE-UA \( n \)-butane, and 9.75 Å for TraPPE-UA \( n \)-dodecane.

Caracciolo et al. observed that the components of the uniquely flexible contribution largely cancel one another. In Monte Carlo calculations, small magnitudes often translate to small standard errors, and we have observed that direct computation of \( T_1 \), for example, is more efficient with regard to minimizing statistical uncertainty than independent computation of the three-molecule chain and \( I_2 \). However, computing \( T_1 \) with one MSMC calculation is slightly more complicated because of the presence of molecule 1′. For the three-site TraPPE-UA models of propane and methanol, it is relatively simple to pair the orientations of molecules 1 and 1′ by restricting the molecules to the same plane and the bisector of their angles to the same vector, as shown in Fig. 1. This roughly minimizes the integrand of \( T_1 \) at each step, and permits the calculation to focus appropriately on the difference of the intramolecular conformations of 1 and 1′. The improvement in sampling efficiency is considerable, and we apply this restriction at all orders considered. One may similarly attempt to pair the orientations of 1 and 1′ for TraPPE-UA \( n \)-butane and larger alkanes, but we have not done so in this work. Additionally, for all of the models considered here, we permute the two root molecules and compute the value of \( T_1 \) via the average shown in Eq. (7). We denote this formulation as \( F_3 \), but it has the same value as \( T_1 \). From this formulation, one can see that the uniquely flexible contribution arises from the correlation of differences in the interactions due to different conformations of molecule 1 (i.e., 1 and 1′):

\[
F_3 = \frac{1}{2} \left \{ (f_{12} - f_{13}) (f_{13} - f_{14}) d\tau_2 d\tau_3 \right \}
\]

Any of the molecules represented in the diagrams may be the root molecule or its alternate because the system is homogeneous. Consequently, we may make our selection in order to maximize the similarity of the integrands of the singly connected and disconnected diagrams, and thus maximize the computational efficiency. To avoid the need for a second alternate of molecule 1 in \( B_4 \), molecule 1′, we employ the expression for \( B_4 \) shown in Eq. (8). \( F_4^A \) has the same value as \( T_4 \), but \( F_4^A \) and \( F_4^R \) differ quantitatively from \( T_2 \) and \( T_3 \), respectively, despite containing the same singly connected diagrams. We compute \( B_n^{NBC} \) using independent MSMC calculations for \( I_2 \), \( F_3 \), and \(-1/2 F_4^A - 3/2 F_4^R - 3/2 F_4^C \):

\[
B_4 = -\frac{1}{8} I_4 + \left( -\frac{1}{2} F_4^A - \frac{3}{2} F_4^R - \frac{3}{2} F_4^C \right) + \frac{5}{2} I_2 F_3 \tag{8}
\]

In \( B_5 \), there are 11 singly connected diagrams consisting of all five molecules, which lead to 11 terms \( F_5 \) analogous to \( F_3 \). We have selected the root molecules as indicated in Eq. (9). We do not show the permutations of molecules 1 and

\[
F_5^A = \frac{1}{2} \left \{ (f_{12} f_{13} - f_{12} f_{14}) (f_{14} - f_{15}) d\tau_2 d\tau_3 d\tau_4 \right \}
\]

\[
F_5^R = \frac{1}{2} \left \{ (f_{12} - f_{13}) f_{13} (f_{14} - f_{15}) d\tau_2 d\tau_3 d\tau_4 \right \}
\]

\[
F_5^C = \frac{1}{2} \left \{ (f_{12} f_{13} - f_{12} f_{14}) f_{13} (f_{14} - f_{15}) d\tau_2 d\tau_3 d\tau_4 \right \}
\]

\[
F_5 = \frac{1}{2} \left \{ (f_{12} - f_{13}) (f_{13} - f_{14}) (f_{14} - f_{15}) d\tau_2 d\tau_3 d\tau_4 \right \}
\]

\[
= \frac{1}{2} \left( \bullet - \bullet + \bullet - \bullet \right)
\]

\[
= \frac{1}{2} \left( \bullet - \bullet + \bullet - \bullet \right)
\]

\[
= \frac{1}{2} \left( \bullet - \bullet + \bullet - \bullet \right)
\]
1′ in Eq. (9), but these are included within our calculations. We compute $B_5^{NRC}$ using independent MSMC calculations for $I_2, I_3, F_3, 1/2F_4^A + 6F_4^B + 3F_4^C$, and the sum of the $F_i$ terms $F_5$, presented in Eq. (9b).

$$B_5 = -\frac{1}{30} I_5 - F_5 + I_2 \left( \frac{1}{2} F_4^A + 6 F_4^B + 3 F_4^C \right)$$
$$+ F_3 \left( 3 I_3 + \frac{9}{2} F_3 - \frac{5}{2} I_2^2 \right)$$ (9)

$$F_5 = \frac{2}{3} F_5^A + 2 F_5^B + 2 F_5^C + \frac{1}{2} F_5^D + 2 F_5^E + 2 F_5^F + 2 F_5^G$$
$$+ F_5^H + 2 F_5^I + 2 F_5^J + \frac{1}{6} F_5^K$$ (9b)

$F_5^A = \text{Diagram}$ (9ba)

$F_5^B = \text{Diagram}$ (9bb)

$F_5^C = \text{Diagram}$ (9bc)

$F_5^D = \text{Diagram}$ (9bd)

$F_5^E = \text{Diagram}$ (9be)

$F_5^F = \text{Diagram}$ (9bf)

$F_5^G = \text{Diagram}$ (9bg)

$F_5^H = \text{Diagram}$ (9bh)

$F_5^I = \text{Diagram}$ (9bi)

$F_5^J = \text{Diagram}$ (9bj)

$F_5^K = \text{Diagram}$ (9bk)

For computations of portions of $B_n$ for TraPPE-UA alkanes, the total number of sampled configurations varied considerably with the size of the molecule and the order $n$. At least five independent calculations were performed for each case, and each independent calculation sampled at least $10^8$ configurations. For computations of $B_n^{NRC}$ for TraPPE-UA methanol, 100 independent calculations of $10^8$ steps were performed for each pairing of temperature and order. For all models considered, an additional 7.5% of the number of samples was devoted to the equilibration period for each independent calculation, and the quoted confidence limits are based on the standard error of the mean of the independent calculations.

The point charges of TraPPE-UA methanol introduce complications, which we treat as in previous work for

FIG. 1. Snapshot of $B_3$ calculation (reference-system Markov chain) for TraPPE-UA propane at 1500 K. Molecule 1 is blue and molecule 1′ (alternate root with same geometric center and paired orientation) is red. Molecules 2 and 3 to left and right are green.
TraPPE-UA methanol $B_2$ and higher-order coefficients of the Gaussian charge polarizable model of water. At separation distances $r$ where the pair interaction is dominated by the dipole-dipole contribution, the sampling weight of $B_2$ (the absolute value of the integrand prior to taking the orientational average) diminishes with $r^{-3}$, a much slower rate of decay than that of the orientationally averaged dipole-dipole interaction, which decays with $r^{-6}$. Applying a coarse orientational average at each step permits us to achieve this appropriately faster rate of decay. For $B_2$, this coarse orientational average is the average of four configurations: the nominal (proposed) configuration, the two configurations where only one of the molecules is “flipped” about its geometric center, and the configuration where both are flipped.

The biconnected parts of higher-order $B_n$ would not benefit from this coarse orientational average because the connectivity sufficiently restricts the separation distances considered. The non-biconnected contributions $B_n^{NRC}$, however, have an even greater need for this procedure than $B_2$. For $B_3^{NRC}$ and $B_4^{NRC}$, we average over $2^3$ and $2^4$ configurations, respectively, where molecule 1 is always flipped with molecule 1 to keep their orientations paired. The coarse orientational average proves insufficient for the linear chain of four molecules belonging to $F_4^{B}$: molecule 2, bonded to the root, and molecule 3, bonded only to molecule 2, are able to migrate together far from the origin and remain far for many consecutive steps. To avoid this sampling inefficiency, we compute $F_4^{B}$ with a slightly different approach, in which molecule 3 is moved to preserve its orientation and position relative to molecule 2, and thus the value of $f_{13}$, whenever molecule 2 is flipped. The presence of $f_{13}$ in $F_4^{C}$ prevents the need for this procedure by anchoring molecule 3 to the origin, but it also precludes its use, because, if the position of 3 were moved with 2, $f_{13}$ could change substantially and prevent cancellation. Additionally, we do not flip the root molecules when computing $F_4^{B}$ as it does not provide any advantage with regard to achieving cancellation, despite providing a less coarse orientational average.

III. RESULTS AND DISCUSSION

A. Virial coefficients

We present virial coefficients $B_n$ and components thereof for the TraPPE-UA models of propane, $n$-butane, $n$-dodecane, and methanol at third through fifth order. Tabulated values are provided in the supplementary material. TraPPE-UA methanol was not considered at fifth order, and the non-biconnected contribution at fifth order $B_5^{NRC}$ was neglected for alkanes with more than five carbons. In Fig. 2, we plot $B_n$ in black, using an asinh scale that facilitates examination of the temperature dependence across the considered temperature range.

We include $B_2$ in Fig. 2(a) as a point of reference, even though it has no uniquely flexible contributions. As the TraPPE-UA alkane chain length increases, and the number of site-site interactions between the two molecules increases, the magnitude of $B_2$ increases. Though TraPPE-UA methanol has three sites, like TraPPE-UA propane, its $B_2$ values are significantly larger, primarily because of long-range Coulombic interactions. The strong orientational dependence resulting from the point charges makes the methanol $B_2$ values especially negative at low temperatures, where highly attractive orientations are strongly preferred. These trends are observed at the higher orders as well.

Where the biconnected contribution $B_4^{BC}$ is discernable from $B_n$ in Fig. 2(b)–2(d), we plot it in red. With the scales selected, the non-biconnected contributions $B_n^{NRC}$ are imperceptible for TraPPE-UA propane at all orders, and that of $n$-butane are visible only at fifth order. $B_n^{NRC}$ is most visible near where $B_n^{BC}$ goes through zero, in part because the scale magnifies differences near zero. To further examine the nature of $B_n^{NRC}$, we have plotted the ratio of it to the magnitude of $B_n$ at third and fourth orders in Figs. 3 and 4, respectively. Overall, the relative significance of $B_n^{NRC}$ to the alkane $B_n$ increases with the chain length and the resulting increase in

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**FIG. 2.** Virial coefficients for TraPPE-UA propane (triangles), $n$-butane (squares), $n$-dodecane (circles), and methanol (diamonds) at (a) second order, (b) third order, (c) fourth order, and (d) fifth order. Symbols are values computed by MSMC and lines are interpolated using the method of Schultz and Kofke (see Ref. 13). White symbols represent total values, while red symbols represent biconnected contributions. Error bars denote 68% confidence limits where they are not smaller than the symbols.
possible intramolecular conformations. Though the propane and methanol models have the same number of sites per molecule, the significance of $B_3^{NBC}$ and $B_4^{NBC}$ is orders of magnitude larger for TraPPE-UA methanol. The strength of the site-site Coulombic interactions of the methanol model is likely responsible.

Caracciolo et al. proved that $B_3^{NBC}$ is always negative, which is what we observe in Fig. 3 at all data points but one: the dodecane data point at 1200 K, which we assume is positive only because of poor precision; its 68% confidence limit extends below the abscissa. For TraPPE-UA propane, the significance of $B_3^{NBC}$ is small but measurable and increases with increasing temperature. Similar to the context of Boltzmann sampling, the molecules become more flexible with increasing temperature, in that a wider range of intramolecular conformations is important with regard to the Mayer functions. $B_3^{NBC}$ for each model considered goes through zero somewhere in this temperature range, and the width of the resulting trough in $B_3^{NBC}/|B_3|$ obscures the effect of temperature for the models other than TraPPE-UA propane.

As a negative quantity, $B_3^{NBC}$ reduces the pressure at a given density and temperature. The sign of $B_3^{NBC}$ is perhaps a reflection of how molecular flexibility permits lower Boltzmann-averaged energies for given center-of-mass configurations. $B_4^{NBC}$ is also negative for TraPPE-UA propane at all considered temperatures, as can be seen in Fig. 4, but becomes positive for TraPPE-UA methanol at a temperature between 500 and 525 K. For TraPPE-UA n-butane and n-dodecane, the uncertainties are too large on $B_4^{NBC}$ to know the sign with confidence. As can be seen in Tables V–VIII of the supplementary material, for all of the models considered, $I_2F_3$ is positive and the remainder of $B_4^{NBC}$ is negative except at the highest temperatures. These contributions are difficult to compute precisely and largely cancel such that the sum is small and has poor precision.
is more difficult to compute to high precision than \( B_n^{NC} \), in part, because the non-biconnected diagrams have contributions from larger swathes of configuration space: the relative lack of connectivity increases the importance of larger separations. This configuration space grows with the number of molecules, and, though calculations for \( B_5^{NC} \) of TraPPE-UA propane and \( n \)-butane were performed, these values are not yet known with confidence, as can be seen in Tables IX and X of the supplementary material.\(^{10}\) We have found that computing \( B_n^{NC} \) together with the portion of \( B_n^{NC} \) that omits disconnected diagrams with more than two parts (e.g., computing \(-1/30\) and \(-F_3\) together) provides a modest improvement in the uncertainties of the total virial coefficient relative to computing these components separately. Including disconnected diagrams with more than two parts would require at least two alternate roots.

B. Vapor-branch spinodals and critical points

As shown in Fig. 5, the VEOS vapor-branch spinodals are almost indiscernible from those computed from the biconnected VEOS (VEOS BC), in which the uniquely flexible contributions are omitted. We terminate these spinodals, the loci of points at which the first derivative of the pressure with respect to density is zero, at the critical point, where the second derivative is also zero. The critical density \( \rho_c \), critical temperature \( T_c \), and critical pressure \( P_c \) for each considered model are presented in Table I for the VEOS and its biconnected approximation. With increasing order, the VEOS estimates of the critical properties approach the critical properties extrapolated from Gibbs-ensemble Monte Carlo simulation data.\(^5,7\) These simulation values are in good agreement with those found experimentally for the modeled fluids.\(^{11,12}\)

To estimate the uncertainty on a VEOS critical property \( x_c \) or a VEOS BC critical property \( x^{BC}_c \), we employ 100 perturbations of the equation of state. Each perturbation is generated by sampling values of \( B_n \) (or \( B^{BC}_n \)) from Gaussian distributions centered at the average and having standard deviation equal to the standard error of this average. We then take the uncertainty of the critical property to be the standard error of its 100 perturbations. Rather than propagating the uncertainties of \( x_c \) and \( x^{BC}_c \) to estimate the uncertainty of the percent contribution of \( B_n^{NC} \) to \( x_c \), we apply this perturbation procedure directly to \((x_c - x^{BC}_c)/x_c\), sampling \( B^{BC}_n \) and \( B_n^{NC} \) independently. From the tabulated values, it can be seen that the differences between the complete and biconnected critical properties are statistically significant for TraPPE-UA propane and methanol at third and fourth order and \( n \)-dodecane at third order.

Where statistically significant, \( B_3^{NC} \) increases VEOS3 estimates of \( \rho_c \), \( T_c \), and \( P_c \) relative to those of VEOS3 BC in accordance with its attractive effect: it decreases the region over which vapor is metastable or stable. For TraPPE-UA \( n \)-dodecane, \( B_3^{NC} \) increases these VEOS3 properties by 1.29(17)\%, 0.47(6)\%, and 1.82(5)\%, respectively, while for TraPPE-UA methanol, it increases these by 3.67(12)\%, 1.04(3)\%, and 4.67(15)\%, respectively. The increases for TraPPE-UA propane critical properties at both third and fourth order are less than 0.01\%. For TraPPE-UA methanol, \( B_3^{NC} \) and \( B_4^{NC} \) together have percent contributions at fourth order that are about half those of \( B_3^{NC} \) at third order. Even though \( B_4^{NC} \), like \( B_3^{NC} \), is negative within this temperature region, the VEOS4 critical point occurs at a lower temperature, where these contributions are smaller.

C. Corrections to previously published TraPPE-UA methanol virial coefficients

Previously published values\(^9\) for TraPPE-UA methanol were computed using an oxygen-hydrogen bond length \( r_{OH} \) of 0.95 Å instead of the value 0.945 Å recommended for the model. This reduced the shielding of the hydrogen’s positive charge by its bonded oxygen, allowing it to have more attractive interactions with other oxygen atoms than it would otherwise. The impact of this additional attraction is significant, indeed more so than the omission of the non-biconnected diagrams, increasing the magnitude of \( B_2 \), \( B_3 \), and \( B_4 \) and their components as shown in Table II. The significance is larger at lower temperatures, where attractive energy wells are most important relative to other configurations, and at higher order, where more molecules are considered. The extended bond more than doubles the magnitude of \( B_4 \) at 275 K.

A plot of the compressibility factor \( Z = P/\rho kT \), computed using the recommended bond length along the saturated
TABLE I. Critical properties for TraPPE-UA models computed through the VEOS, computed through the bi-connected VEOS (VEOS BC), or extrapolated from the simulation data, and critical properties for the modeled fluids determined by experiment. Values in parentheses are 68% confidence limits on the rightmost digit(s).

<table>
<thead>
<tr>
<th>Equation of state</th>
<th>( \rho_c ) (mol/L)</th>
<th>( T_c ) (K)</th>
<th>( P_c ) (MPa)</th>
<th>% contribution of ( B_{nNBC} )</th>
<th>( \rho_c ) (mol/L)</th>
<th>( T_c ) (K)</th>
<th>( P_c ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>VEOS3</td>
<td>5.4228(18)</td>
<td>392.85(9)</td>
<td>5.904(3)</td>
<td>0.00280(11)</td>
<td>0.00131(5)</td>
<td>0.00411(16)</td>
<td></td>
</tr>
<tr>
<td>VEOS3 BC</td>
<td>5.4227(17)</td>
<td>392.84(11)</td>
<td>5.904(3)</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>VEOS4</td>
<td>4.179(7)</td>
<td>363.4(2)</td>
<td>4.405(8)</td>
<td>0.0040(13)</td>
<td>0.0017(4)</td>
<td>0.0054(16)</td>
<td></td>
</tr>
<tr>
<td>VEOS4 BC</td>
<td>4.179(7)</td>
<td>363.4(2)</td>
<td>4.405(8)</td>
<td></td>
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</tr>
<tr>
<td>VEOS5</td>
<td>4.22(5)</td>
<td>364.2(1.0)</td>
<td>4.44(5)</td>
<td>1.0(1.1)</td>
<td>0.2(3)</td>
<td>0.9(1.0)</td>
<td></td>
</tr>
<tr>
<td>VEOS5 BC</td>
<td>4.22(3)</td>
<td>363.4(6)</td>
<td>4.4(1)</td>
<td></td>
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<tr>
<td>Simulation(^a)</td>
<td>5.01(7)</td>
<td>368(2)</td>
<td>4.4(1)</td>
<td></td>
<td></td>
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<tr>
<td>Experiment(^b)</td>
<td>4.99(7)</td>
<td>369.83(10)</td>
<td>4.24(10)</td>
<td></td>
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<tr>
<td>n-Butane</td>
<td></td>
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\(^a\) Reference 7.  
\(^b\) Reference 11.  
\(^c\) Reference 6.  
\(^d\) Reference 12.
FIG. 6. The compressibility factor $Z$ for TraPPE-UA methanol along the saturated vapor line assuming the saturated vapor densities and temperatures determined for the model by Gibbs-ensemble Monte Carlo simulation (see Ref. 6). These simulation data are represented with circles. VEOS2 values are represented with white diamonds, VEOS3 values with white triangles, VEOS3 BC values with red triangles, VEOS4 values with white squares, and VEOS4 BC values with red squares. The compressibility factor for methanol along its saturated vapor line (see Ref. 14) is represented with a black curve.

The uniquely flexible contributions improve the VEOS3 and VEOS4 estimates of the model’s compressibility factor.

IV. CONCLUDING REMARKS

The uniquely flexible contributions to the virial coefficients are in many instances negligible or small, but they can be significant and must be examined to ensure accuracy in calculated virial coefficients. Even when they are small, it can be difficult to compute them to the same precision as the biconnected contributions. We will continue to develop techniques that facilitate their computation in future work.

ACKNOWLEDGMENTS

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10See supplementary material at http://dx.doi.org/10.1063/1.3657773 for tabulated values of the virial coefficients and components thereof.