

Mayer-sampling Monte Carlo calculations of methanol virial coefficients

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We present virial coefficients of up to fourth order computed by Mayer-sampling Monte Carlo for three pair potentials of methanol: one parameterized to reproduce vapour-liquid coexistence and two others parameterized to reproduce a quantum pair potential. We compare the resulting second and third virial coefficients to experimental values available in the literature. We further examine the virial coefficients within the context of the virial equation of state, computing vapour-branch spinodals, critical points, and saturated-vapor compressibility factors. The results of the three potentials differ qualitatively, reflecting the primary differences in the parameterization schemes.

Keywords: virial coefficient; methanol; Mayer sampling

1. Introduction

The ability of an intermolecular potential to reproduce the virial coefficients B_n of the fluid it describes is an important measure of its efficacy, as these quantities encapsulate the temperature-dependent behavior within clusters of n molecules. Connection with bulk properties is afforded by the virial equation of state (VEOS), shown in Equation (1), which relates the pressure P to the temperature T and density ρ (k is Boltzmann's constant). Analysis of the virial coefficients and properties computed from the VEOS can provide meaningful guidance as to how the molecular model could be improved.

$$\frac{P}{\rho k T} = 1 + \sum_{n=2}^{\infty} B_n(T) \rho^{n-1} \quad (1)$$

Estimating fluid properties, such as the critical temperature, from the VEOS is trivial once the B_n values are known, but computation of these quantities remains a time-consuming task. B_n is an integral over the configuration space of the n molecules, a domain that is especially complex when the model employed is not spherically symmetric. Mayer-Sampling Monte Carlo (MSMC) has enabled calculation of higher-order virial coefficients than previously possible for a variety of complex potentials, including virial coefficients of up to sixth order for several water models with fixed point charges [1] and up to fifth order for the Gaussian charge polarisable model (GCPM) of water [2].

Here, we apply the method to compute virial coefficients for three multisite pair potentials of methanol. The first model belongs to the class of transferable potentials for phase equilibria-united atom (TraPPE-UA) [3, 4], which is regarded as the best available transferable model for alcohols along the saturation curve [5]. The

other two models were published by Rowley, Tracy, and Pakkanen in 2006 [6] and are largely untested. To our knowledge, this is the first attempt to calculate any thermodynamic properties using the RTP models of methanol.

One of the RTP models includes fixed point charges like TraPPE-UA methanol, while the other includes no electrostatic interactions. We refer to these models as RTP (PCs) and RTP (no PCs), respectively. Among other differences, TraPPE-UA methanol consists of three united-atom sites and includes a bending potential, while the RTP models are rigid and have a satellite site as well as an explicit site for each atom. In addition to the Coulombic interactions, sites on different TraPPE-UA methanol molecules interact through Lennard-Jones potentials, whereas the RTP models employ Morse potentials.

What most differentiates TraPPE-UA methanol and the RTP models is not the number of sites or the potential formulations, but rather the way in which the parameters for these models were fit. TraPPE-UA methanol is a semi-empirical model. Most of its parameters are borrowed from other models like the optimized potential for liquid simulations-united atom (OPLS-UA) model, and the parameters in the Lennard-Jones interactions involving oxygen were optimized through Gibbs-ensemble MC (GEMC) calculations to reproduce experimental vapor-liquid coexistence curves. The RTP models were developed from first principles alone: site-site Morse potentials were parameterized by fitting, in a least squares sense, to quantum-mechanical (QM) dimer energies over a range of separation distances and for a variety of relative orientations.

2. Mayer-sampling Monte Carlo

Mayer-sampling Monte Carlo has been described in detail elsewhere [1], but here we review a few key concepts. Analogous to the development of a free-energy perturbation calculation, one multiplies and divides the integral of interest Γ by a known reference quantity Γ_{ref} . Within the context of a virial-coefficient calculation, Γ_{ref} is typically chosen as the hard-sphere B_n . One then formulates the ratio of Γ to Γ_{ref} as a ratio of ensemble averages by introducing a sampling weight π . Configurations which have a larger integrand γ and thus a larger contribution to the integral, are more important to the calculation. Accordingly, π is selected to be the absolute value of γ . Singh & Kofke (2004) named the method *Mayer sampling* because the integrands of virial coefficients are composed of Mayer functions [7]. This direct-sampling formalism is summarized in Equation (2).

$$\Gamma = \Gamma_{ref} \frac{\langle \gamma / \pi \rangle}{\langle \gamma_{ref} / \pi \rangle} \quad (2)$$

Overlap sampling was later found to be more efficient and robust when a hard-sphere reference is employed [1], and has been used in subsequent works [2, 8]. It employs two sampling weights, one computed with the potential of interest and the other with the reference potential. The MSMC steps are apportioned between the two systems employed in the calculation so as to minimize the standard error. Generally, the number of steps allocated to the simulation governed by hard spheres is slightly more than one percent of the total.

Here we employ the overlap-sampling formalism of MSMC to compute second, third, and fourth virial coefficients for each methanol model at temperatures spanning a range of 275 K to 700 K. For each order and temperature, we employed

one hundred runs of a billion Monte Carlo steps. Each run was performed using Java on one node of a 2x3.2GHz Intel Xeon "Irwindale" processor. The systems' small system size (n molecules) and short equilibration period make parallelization trivial to implement via independent MC series.

As the order of the virial coefficient increases, so does the number of pair interaction energies that must be computed at each sampled configuration. Accordingly, one step of a B_4 calculation requires about twice as much time as one step of a B_3 calculation. Specifically, one run of a billion MSMC steps for TraPPE-UA methanol requires 10 hours for B_4 and 5.5 hours for B_3 . For each order, runs for both of the Rowley models are about three times longer because of the larger number of site-site interactions required to calculate molecular interaction energies.

MSMC calculations do not employ formal bounds on configuration space. Rather the sampling weight, which diminishes with increasing separation distances, effectively bounds the important region of configuration space. Using the absolute value of the integrand as the sampling weight, calculations of B_2 for models with point charges can, for some seeds, visit far too many configurations with long separation distances where the orientation-averaged interaction energy is negligible. Benjamin, Schultz, and Kofke (2009) found that employing the absolute value of a rough orientational average of the integrand as the sampling weight, rather than the absolute value of the integrand, remedies this inefficiency [2]. The averaging introduces no approximation, as the considered orientations have equal volumes in phase space. More details regarding the method can be found in their paper, where it was applied to facilitate calculation of fifth and lower virial coefficients for GCPM water. Because of this procedure, one step of a B_2 calculation requires more time than

one step of a B_3 calculation: a TraPPE-methanol B_2 calculation of a billion MSMC steps requires about seven hours on the type of processor described previously.

3. Results and discussion

We first present the virial coefficients computed by MSMC for each model, and we compare the second- and third-order values to experimental values reported in the literature. We indirectly assess the quality of the fourth (and lower-order) coefficients by computing quantities from the VEOS that can also be compared to experimental values: namely, the critical point and the saturated-vapor compressibility factors.

3.1 Virial Coefficients

The second, third, and fourth virial coefficients computed by MSMC are tabulated in (Table 1) for TraPPE-UA methanol, (Table 2) for RTP (no PCs) methanol, and (Table 3) for RTP (PCs) methanol. The values in parentheses are the 67% confidence limits for the coefficients. Upon increasing the order of the coefficient, the ratio of this standard error to the value of the coefficient increases by about an order of magnitude given the same number of runs.

The virial coefficients differ markedly from model to model and order to order, often by several orders of magnitude, but they follow the common trend of being large, negative, and rapidly changing at low temperatures, while being smaller and slowly changing at higher temperatures. To interpolate between the values, we employ the method developed by Schultz and Kofke [9], which takes advantage of this general behaviour. We have plotted the simulation results along with the interpolated values in (Figure 1) for B_2 , (Figure 2) for B_3 , and (Figure 3) for B_4 . The

coefficients are plotted on an inverse hyperbolic-sine scale to facilitate comparison across both temperature regimes on a single plot.

The differences in the parameterization procedures for each model are clearly manifested in the calculated values of the second virial coefficient. The RTP models, fit to pair information only, yield values that generally match the experimental correlation of Tsonopoulos and Dymond [10] more closely than those computed for TraPPE-UA methanol. At the lower temperatures considered, the performance of RTP (no PCs) is particularly good. This result raises concerns about the quality of the Coulomb potentials of the other models, as strongly directional interactions are more significant at lower temperatures. We note that in the plots of the RTP and QM potential energies published by Rowley *et al.* (2006) [6], one can see that the RTP (no PCs) potential is generally much weaker than both the QM and the RTP (PCs) potentials at separation distances larger than six Angstroms, not a particularly long separation distance considering the well depths. Still, this marked weakness is likely a result of the absence of Coulomb site-site potentials, which would persist at larger separation distances than Lennard-Jones or Morse interactions.

Analogous to how Boltzmann averages of a dipole-dipole interaction energy over relative orientations are more attractive at lower temperatures (configurations that minimize the potential energy are more favored), the inclusion of appropriate orientation-dependent electrostatic interactions should make the virial coefficients more negative at lower temperatures. As the temperature increases, the sampling of orientations becomes more random, mitigating this effect for a model with strongly directional interactions like the Coulombic interactions of TraPPE-UA methanol.

TraPPE-UA methanol is parameterized to reproduce bulk liquid-vapor coexistence data, such that multibody effects are accounted for in the pair potential.

Specifically, the fixed charges of TraPPE-UA methanol result in a dipole moment of 2.23 D at the equilibrium bond angle. This and its other parameters are selected to strike a balance between vapour and liquid properties, inevitably resulting in a pair interaction energy that is too attractive to describe interactions in the vapor accurately, especially at lower temperatures. Thus, it is not surprising that the B_2 values of TraPPE-UA methanol values are more negative over much of the temperature range than the experimental correlation of Tsonopoulos and Dymond [10], which represents experimental data very well [11-15]. Benjamin, Singh, Schultz, and Kofke observed the same B_2 behavior in their examination of water models with fixed point charges selected in a similar fashion [1].

The second virial coefficient of RTP (no PCs) is appropriate at the lower temperatures but becomes too negative as temperature increases, perhaps because the potential is less sensitive to orientation. Indeed, the virial coefficients of RTP (no PCs) methanol and TraPPE-UA methanol cross paths between 450 and 525 K, implying that that the TraPPE-UA potential is more attractive than RTP (no PCs) at configurations important at lower temperatures, and more repulsive at configurations important at higher temperatures.

The RTP (PCs) model yields markedly more positive coefficients than the other models at all orders considered, and in this respect RTP (PCs) is clearly the potential with the most overall repulsive nature. It employs a distribution of point charges with a dipole moment of 2.07 D, a value seven percent smaller than the dipole moment of relaxed TraPPE-UA methanol, which explains, at least in part, why the RTP (PCs) values are more positive than those of TraPPE-UA methanol. It is more difficult to understand why the B_2 values of RTP (PCs) methanol are more positive than those of experiment and RTP (no PCs). In the plots published by Rowley *et al.*

(2006) [6], RTP (PCs) is consistently more repulsive than RTP (no PCs) for routes in which the oxygens approach one another, but other approach routes yield mixed results. The RTP (PCs) dipole moment is larger than the value of 1.70 D determined experimentally for methanol vapour [16], but we do not know what values are appropriate for strongly interacting methanol dimers. If the Coulomb potential is, on average, too attractive, the Morse component of potential must be overcompensating for it.

The agreement of the TraPPE-UA B_3 values with those determined experimentally by Kell and MacLaurin (1969), Bich *et al.* (1984), and Olf *et al.* (1989) between 400 K and 500 K is remarkable [11-13]. At these and lower temperatures, TraPPE-UA B_3 values are even larger relative to the RTP values than was the case for B_2 , and the difference is amplified further at fourth order. Clearly, the effect of the more attractive pair potential compounds as the order of the coefficient (and the number of pair interactions) increases.

3.2 Vapor-branch spinodals and critical points

From the third- and fourth-order virial equations of state (VEOS3 and VEOS4), we have computed spinodal curves for each potential up to the critical point, plotted in (Figure 4). We do not do the same for VEOS3 of methanol, due to the amount of scatter in the experimentally determined B_3 values. We do not plot any part of the liquid branch of the spinodal because it is often inaccurate to the point of being unphysical; the inapplicability of the VEOS to the liquid phase prevents computation of the binodal as well. We have included the critical point of methanol, determined experimentally, and the critical point of TraPPE-UA methanol, determined through GEMC and scaling arguments [3]. To our knowledge, the critical

points of the RTP models have not been computed, nor have other spinodal points of any of the models we consider.

The spinodals computed from the truncated VEOSs differ greatly from model to model, reflecting the differences in the virial coefficients. The RTP (PCs) model, which has the most positive virial coefficients, yields significantly lower spinodal temperatures, consistent with the expectation that a more repulsive potential would yield vapor metastable at lower temperatures. Similar to the behavior observed for the virial coefficients, the VEOS3 and VEOS4 spinodals of the RTP (no PCs) model and the TraPPE-UA model cross paths between 450 and 500 K.

For models of simple fluids, such as the Lennard-Jones potential, low-order VEOSs can yield reasonable estimates of the critical temperature. For example, VEOS4-LJ yields a critical temperature within 1% of the correct value [17]. By contrast, VEOS4 of TraPPE-UA methanol underestimates the critical temperature of the model, 502(2) K [3], by 7.2%. Poorer agreement for a particular order of VEOS is to be expected for models of associating fluids, as higher-order interactions are more important. With that caveat noted, our low-order estimates indicate that the RTP (no PCs) model would likely overpredict the critical temperature, while the RTP (PCs) model would underpredict it.

3.3 Saturated-vapor compressibility factors

We compute VEOS compressibility factors along the vapor branch of the binodal as this provides us with another means to gauge the accuracy of the models: the liquid-vapor coexistence curve has been determined experimentally for methanol [18, 19] and by GEMC for TraPPE-UA methanol [3]. In (Figure 5), we have plotted the corresponding compressibility factors, as well as those computed from truncated

VEOSs for each model and for methanol. The methanol VEOS values employ the B_2 and B_3 values of Bich *et al.* (1984) [12], available at 356.15 K and higher, as well as the B_2 values of Boyes *et al.* (1992) [14]), which extend the temperature range of VEOS2 down to 280 K.

The results for methanol and for the RTP models were computed assuming the experimentally determined saturation temperatures and vapor densities, while those of TraPPE-UA methanol were computed assuming the saturation temperatures and vapor densities determined for the model by GEMC. Only the standard errors in the virial coefficients, and not the standard errors in the GEMC saturated-vapour densities, are used to compute the confidence limits of the VEOSn compressibility factors. These confidence limits are smaller than the markers employed.

At the lower densities and temperatures, VEOS-RTP (no PCs) reproduces the compressibility factors of methanol the best, reflecting the good agreement between the B_2 values of the model and methanol at low temperatures. Below 400 K, there is strong agreement (to within about 0.2%) between the results of the different orders of VEOS for each of the RTP models, indicating that third- and fourth-order contributions are minute. From the two experimental VEOS3 data points between 350 K and 400 K, one can see that these models underestimate the third-order contribution there.

At the smallest densities considered, where the experimental VEOS2 results agree quite well with the bulk, one would not anticipate significant contributions from higher-order terms. However, even at the lowest density, the fourth-order contribution of TraPPE-UA methanol is non-negligible: the fourth-order compressibility factor differs from the second-order result by more than 3%, a difference that is too large to be the result of standard error. At the three lowest

densities, all of the VEOS results for TraPPE-UA methanol lie within the error bars of the GEMC data, but the VEOS4 results appear to diverge from the GEMC data, indicating that even higher-order contributions could be significant at these densities. The only positive virial coefficient for TraPPE-UA methanol at the saturation conditions considered is B_4 at 475 K, such that all of the other values serve to reduce the compressibility factor. Presumably higher-order coefficients become positive at lower temperatures.

As the density increases, the VEOS results of the RTP models diverge from the experimental results. At the highest density considered, VEOS4 of TraPPE-UA methanol provides the best estimate of the experimental compressibility factor, but the value is outside the error bars of the GEMC result. At this density, the VEOS2 and VEOS3 results for TraPPE-UA methanol are highly inaccurate. In particular, the third-order result yields a negative pressure and is off the scale of the plot.

The GEMC results for TraPPE-UA methanol yield compressibility factors that are always smaller than those of methanol, which is another indication that the potential is too attractive. Similarly, the VEOS compressibility factors of RTP (PCs) methanol are all too high, reflecting a potential that is too repulsive. The change in the RTP (no PCs) values from being too high to too low between 400 and 450 K could be caused by the absence of strongly orientation-dependent electrostatic interactions.

4. Conclusions

We have presented virial coefficients of up to fourth order for three models of methanol and have employed these values to compare low-density properties for each. The virial coefficients consolidate the spatial dependence of the potentials,

conclusively demonstrating that the RTP (PCs) model is, overall, more repulsive than both methanol and the RTP (no PCs) model at relevant configurations. The RTP model without point charges appears to generally reproduce experimental values the best at low temperatures (and densities), but its poorer performance at higher temperatures is likely caused by the absence of electrostatic interactions of some type.

Across the range of temperatures considered, the results for TraPPE-UA methanol reflect a pair potential that is too attractive. The significant fourth-order contribution of TraPPE-UA methanol at densities three orders of magnitude smaller than the critical density appears to be unphysical but is not unexpected for a model with fixed point charges developed to reproduce vapour-liquid coexistence. The inaccuracy of the compressibility factors computed from VEOS2 and VEOS3 of TraPPE-UA methanol at the highest density point considered reflects more poorly upon VEOS2 and VEOS3 than it does upon the model. Generally, the more important multibody interactions are, the less effective a low-order VEOS is.

Though TraPPE-UA methanol overpredicts the importance of multibody interactions at the conditions considered, both RTP models appear to underpredict their importance. This underprediction is likely a direct result of their parameterization employing QM potential energies of pairs and not higher-order clusters. However, the large differences in the results of the two RTP models demonstrate the difficulty of developing effective pair potentials from a dimer QM potential-energy surface, and diminish the appeal of applying the fitting procedure to the even more complex surfaces of higher-order clusters. Because of the severity of the differences in the results of the two RTP models, we can conclude little about the quality of the QM potential employed.

Virial coefficients could facilitate a more systematic approach to the parameterization of potentials from QM data. Acknowledging current computational barriers, the virial coefficients seamlessly connect molecular-level detail with bulk vapour behaviour, and at low orders they can be compared directly with experimental data. Most interestingly, within the context of Mayer sampling, the virial coefficients provide quantitative guidance as to what part of the QM potential-energy surface would be most important to reproduce for application of the fitted potential at a given temperature.

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Table 1. Virial Coefficients for TraPPE-UA methanol [3] as calculated by Mayer-sampling Monte Carlo.

T (K)	B_2 (L/mol)	B_3 (L/mol) ²	B_4 (L/mol) ³
275	-9.4409(12)	-1851(3)	$-5.78(7) \times 10^6$
300	-4.2424(4)	-205.87(18)	$-1.004(10) \times 10^5$
325	-2.2400(2)	-33.28(3)	$-3.58(3) \times 10^3$
350	-1.33750(13)	-7.106(4)	-210.0(1.4)
375	-0.87688(6)	-1.8637(10)	-17.75(11)
400	-0.61679(3)	-0.5612(3)	-1.819(15)
425	-0.45757(2)	-0.18364(12)	-0.183(3)
450	-0.353480(16)	-0.06051(5)	0.0049(6)
475	-0.281570(14)	-0.01689(3)	0.01680(16)
500	-0.229630(9)	-0.000866(13)	0.01116(6)
550	-0.160690(6)	0.006704(6)	0.003438(10)
600	-0.117550(5)	0.006586(3)	0.001083(3)
650	-0.088273(3)	0.0054715(16)	0.0003638(13)
700	-0.067177(3)	0.0044745(10)	0.0001275(7)

Note: Numbers in parentheses represent the 67% confidence limits (standard error of the mean) for the rightmost digits of the value.

Table 2. Virial Coefficients for RTP (no PCs) methanol [6] as calculated by Mayer-sampling Monte Carlo.

T (K)	B_2 (L/mol)	B_3 (L/mol) ²	B_4 (L/mol) ³
275	-2.9040(3)	-23.644(10)	-1250(6)
300	-1.71220(14)	-5.2180(19)	-95.0(3)
350	-0.80432(4)	-0.46733(18)	-1.828(5)
400	-0.48129(2)	-0.06228(4)	-0.0936(3)
450	-0.329320(12)	-0.005591(11)	-0.00794(3)
500	-0.243840(8)	0.004106(4)	-0.000618(7)
550	-0.189660(7)	0.005354(2)	0.0001284(19)
600	-0.152400(5)	0.0049373(12)	0.0001546(11)
650	-0.125180(4)	0.0042856(8)	0.0001105(5)
700	-0.104420(4)	0.0036995(6)	0.0000785(3)

Note: Numbers in parentheses represent the 67% confidence limits (standard error of the mean) for the rightmost digits of the value.

Table 3. Virial Coefficients for RTP (PCs) methanol [6] as calculated by Mayer-sampling Monte Carlo.

T (K)	B ₂ (L/mol)	B ₃ (L/mol) ²	B ₄ (L/mol) ³
275	-1.81160(12)	-9.252(4)	-134.4(9)
300	-1.07210(6)	-1.7985(10)	-6.58(6)
350	-0.48759(2)	-0.09011(10)	0.1030(9)
400	-0.273040(10)	0.01090(2)	0.02389(7)
450	-0.171210(7)	0.013816(7)	0.004619(12)
500	-0.114170(4)	0.010052(3)	0.000990(3)
550	-0.078493(3)	0.0071317(15)	0.0002104(13)
600	-0.054344(2)	0.0052673(10)	0.0000325(6)
650	-0.0370570(19)	0.0040952(7)	-0.0000013(3)
700	-0.0241430(18)	0.0033442(5)	0.0000007(2)

Note: Numbers in parentheses represent the 67% confidence limits (standard error of the mean) for the rightmost digits of the value.

Figure 1. Temperature dependence of B_2 for each model, plotted as $\sinh^{-1}(B_2\rho_c)$ versus temperature, where ρ_c is the experimental critical density of methanol (0.272 g/mL). Solid symbols are values computed by MSMC. Lines connecting MSMC data points were interpolated using the method of Schultz and Kofke [17]. Open symbols are experimental data [11-15].

Figure 2. Temperature dependence of B_3 for each model, plotted as $\sinh^{-1}(B_3\rho_c^2)$ versus temperature. Solid symbols are values computed by MSMC. Lines connecting MSMC data points were interpolated using the method of Schultz and Kofke [17]. Open symbols are experimental data [11-13, 15].

Figure 3. Temperature dependence of B_4 for each model, plotted as $\sinh^{-1}(10B_4\rho_c^3)$ versus temperature. Solid symbols are values computed by MSMC. Lines connecting MSMC data points were interpolated using the method of Schultz and Kofke [17].

Figure 4. Spinodals computed from VEOS3 and VEOS4 for each model up to the computed critical point.

Figure 5. Compressibility factors computed along the saturated vapor line.

Note: Compressibility factors for VEOSn-TraPPE-UA methanol were computed assuming the saturated vapour densities and temperatures

determined for TraPPE-UA methanol by GEMC. The saturation temperatures are listed beneath the data.

Note: Compressibility factors for VEOSn of both RTP models were computed assuming the NIST saturated vapour densities and temperatures of methanol [18, 19]. The saturation temperatures are listed above the data.

Note: The uncertainties in the computed compressibility factors resulting from standard errors in the computed virial coefficients are smaller than the markers employed.





