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Prediction and Refinement of High-Order Virial Coefficients for a Hard-Sphere System *

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The $n^{\rm th}$ virial coefficient for a hard-sphere system is expressed as the sum of n^2 and a remainder. When $n \geq 3$, the remainders of the virials can be accurately expressed with Pade-type functions of n. The maximum deviations are only 0.039–0.053%, which are much better than the existing approaches. By using the predicted virials, the compressibility factors of the hard-sphere system can be predicted very accurately in the whole stable fluid region, and those in the metastable fluid region can also be well predicted up to a packing fraction of 0.545. The simulated B_7 and B_{10} are found to be inconsistent with the other known virials, and thus they are refined to be 53.2467 and 105.042, respectively.

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Despite its simple intermolecular potential, the hard-sphere system captures some typical phase behavior features of real systems, such as stable fluids, metastable fluids, solids, glass states, and random close-packed states,[1−3] and thus it is commonly used as a reference system in constructing thermodynamic or statistical mechanics models for real systems.[4,5]

The virial series expansion for the hard-sphere system is typically expressed as

$$Z = \frac{PV}{RT} = \sum_{n=1}^{\infty} B_n \eta^{n-1}$$
$$= 1 + B_2\eta + B_3\eta^2 + B_4\eta^3 + B_5\eta^4 + \cdots, \qquad (1)$$

where Z, P, V, T, R, η and B_n are the compressibility factor, pressure, molar volume, temperature, Avogadro constant, packing fraction and the $n^{\rm th}$ virial coefficient reduced by the excluded volume of hard-spheres, respectively. For the hard-sphere system, the first four virial coefficients ($B_1 - B_4$) can be derived analytically,[6] and their values are 1, 4, 10 and 18.36476838$\cdots$, respectively. The other virial coefficients need to be calculated numerically, where the fifth to tenth virials have been determined using Monte Carlo simulations (Table 1).[7,8] If only these virials are used to predict the compressibility factors of a pure fluid, the maximum deviation from the simulated results in the isotropic region is over 2%, which is inadequate for accurate theoretical or practical research. In addition, we found that there is obvious inconsistency among the known values of the first ten virials. In order to obtain accurate estimation of higher-order virials, various approaches have been proposed, e.g., Pade approximants,[9] Levin approximants,[10] EOS using simulated compressibility factors,[11] and many other approaches.[9] Most of these approaches are capable of accurate or reasonable prediction of the closest one or two higher-order virials that are not used in parameterization, but the accuracy of predicted virials decreases rapidly as the order increases (Fig. 1).[7−9,11−19] Additionally, the approaches mentioned above also have other problems. For example, the commonly used Pade approximants often overestimate high-order virials not used in parameterization. If we extract high-order virials from simulated compressibility factors, the deviation will increase rapidly with increasing order, because high-order virials are very sensitive to the deviations of compressibility factors.

Table 1. Simulated values and uncertainties of $B_5 - B_{10}$. The uncertainties in brackets are given the last significant number(s).

n	B_n	
	Labik *et al.*[7]	Clisby and McCoy[8]
5	28.22445(10)	28.2245(3)
6	39.81550(36)	39.81515(93)
7	53.3413(16)	53.34442(37)
8	68.540(10)	68.538(18)
9	85.80(8)	85.813(85)
10		105.78(39)

In order to obtain reliable high-order virials that are adequate to construct a highly accurate EOS for a hard-sphere fluid, one has to resort to other approaches. In this work, we report a class of very accurate approaches for the prediction of high-order virials, and correct the inconsistency among the first to tenth known virials.

It is found that there is a well-behaved relationship between the known virials and their orders, which can be used to correlate or predict high-order virials. The known virials $B_1 - B_{10}$ can be roughly approximated by n^2, and the remainders only vary from 0 to 6 (Fig. 2). For this reason, any $n^{\rm th}$ virial coefficient

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can be expressed as

$$B_n = n^2 + \Delta B_n, \tag{2}$$

where ΔB_n is the remainder of the n^2 approximation. Among the remainders, $\Delta B_1 = \Delta B_2 = 0$, and the others behave as a monotonically increasing function of n.

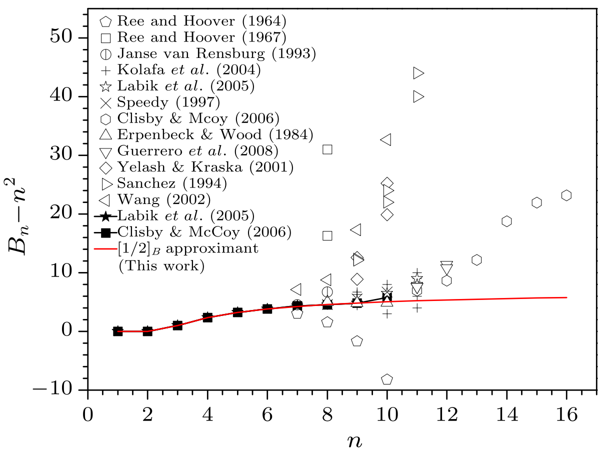

Fig. 1. Comparison of the remainders from analytical expression and computer simulation with those estimated by different approaches. Solid and opened symbols denote the simulated (or analytical) values and the estimated values, respectively. The estimated values are only given for $n \ge 7$.

As can be seen from Fig. 2, the value of B_{10} is obviously inconsistent with the overall trend of $B_3 - B_9$. Furthermore, B_7 is also slightly inconsistent with other virials. Since $\Delta B_n \ll n^2$, the inconsistency is greatly weakened in the $B_n - n$ diagram. This may be the principal reason why there is no report on this inconsistency. We found that the deviations due to the inconsistency are much larger than the uncertainties given by the original authors.[7,8] One may think that the positive deviations of B_7 and B_{10} from the overall trend of other virials may arise from the singularity of the hard-sphere system found in the fluid-solid transition region (which has a positive contribution to Z and B_n). However, if the singularity has a perceptible contribution to B_7 and B_{10}, it should also have a comparable contribution to B_8, B_9 and other virials, because the abnormality of B_7 and B_{10} is too weak to explain the singularity. On the other hand, there is excellent agreement between $B_3 - B_6$, B_8 and B_9, which is sufficient to rule out the singular contribution. In other words, the inconsistency should come from the uncertainties of simulations. The following points also support this conclusion: (1) In the past fifty years, the simulated values of B_7 vary from 56.5 ± 1.6[12] to 56.1 ± 2.5,[20] 53.7 ± 0.8,[21] 53.70 ± 0.33,[22] 53.54 ± 0.29,[14] 53.436 ± 0.090,[23] 53.3444 ± 0.0037[8,24] and 53.3413 ± 0.0016,[7] where some subsequently simulated values are not in the uncertainty ranges of the older results. That is, the uncertainty in simulated B_7 has been underestimated more than once. Nevertheless, the deviation of B_7 due to the inconsistency is still in the uncertainty ranges of some simulated results, such as 53.54 ± 0.29[14] and 53.7 ± 0.8.[21] (2) The uncertainty in B_{10} is very likely underestimated. According to Labik *et al.*,[7] the expected error in B_{10} estimated by extrapolating the latest (and also most accurate) values of $B_5 - B_{10}$ is about ± 1, which is much larger than the uncertainty (± 0.39) reported by Clisby and McCoy.[8,24]

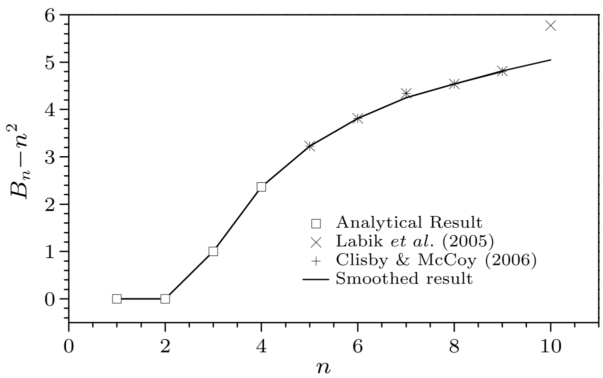

Fig. 2. The remainder $B_n - n^2$ as a function of n.

On the other hand, the singularity in the fluid-solid transition must have a perceptible contribution to some virials, although we do not know its exact range of order or its exact magnitude at the present time. For convenience, we do not consider the singular contribution to B_n. In this way, we can assume that the non-zero values of ΔB_n behave regularly as a function of order. This assumption proves to be valid if we are only interested in the high-order virials that are necessary and sufficient to construct a highly accurate EOS.

Table 2. Parameters from the constraints of $B_4 - B_6$.

$\frac{b_i}{a_i}$	$[1/1]_B$	$[1/2]_B$	$[2/1]_B$
a_1	$0.2937638 \times 10^{+0}$	$0.2935558 \times 10^{+0}$	$0.2934069 \times 10^{+0}$
a_2		0.4378624×10^{-4}	
b_1	$0.2059452 \times 10^{+1}$	$0.2059063 \times 10^{+1}$	$0.2058915 \times 10^{+1}$
b_2			$-0.3068293 \times 10^{-3}$

We find that the non-zero remainders can be well formulated with Pade-type functions of order:

$$\Delta B_n = [L/M]_B = \frac{1 + \sum_{l=1}^{L} b_l (n-3)^l}{1 + \sum_{m=1}^{M} a_m (n-3)^m}, \quad (n \ge 3), \tag{3}$$

where $[L/M]_B$ is the approximant symbol for B_n. In order to predict B_7 and higher-order virials, only $B_3 - B_5$ or $B_3 - B_6$ can be used to constrain the approximants. It is found that the $[1/1]_B$, $[1/2]_B$ and $[2/1]_B$ type approximants can give accurate prediction of $B_7 - B_{10}$. Since the uncertainties of virials simulated by Labik *et al.*[7] are obviously smaller than those of Clisby and McCoy,[8] we use the results of Labik *et al.*[7] to constrain the three approximants. The parameters are given in Table 2.

Table 3. Parameters from the constraints of $B_4 - B_9^*$. B_7 takes the modified value.

b_i/a_i	$[2/2]_B$	$[2/3]_B$	$[3/2]_B$	$[3/3]_B$
a_1	$0.2890695 \times 10^{+0}$	0.9356564×10^{-1}	0.9341709×10^{-1}	$-0.6817809 \times 10^{-1}$
a_2	$-0.1275538 \times 10^{-2}$	$-0.5866498 \times 10^{-1}$	$-0.5867900 \times 10^{-1}$	$-0.7393487 \times 10^{-1}$
a_3		$-0.8716818 \times 10^{-5}$		0.9482139×10^{-2}
b_1	$0.2054580 \times 10^{+1}$	$0.1859074 \times 10^{+1}$	$0.1858925 \times 10^{+1}$	$0.1697400 \times 10^{+1}$
b_2	$-0.9245081 \times 10^{-2}$	$-0.4117940 \times 10^{+0}$	$-0.4120705 \times 10^{+0}$	$-0.7127892 \times 10^{+0}$
b_3			0.6109191×10^{-4}	0.6651676×10^{-1}

Table 4. $B_5 - B_{16}$ predicted from different approximants. Underlined values: known virials (simulated or refined).

n	$[1/1]_B$	$[1/2]_B$	$[2/1]_B$	$[2/2]_B$	$[2/3]_B$	$[3/2]_B$	$[3/3]_B$
5	$\underline{28.22445}$	$\underline{28.22445}$	$\underline{28.22445}$	$\underline{28.22445}$	$\underline{28.22445}$	$\underline{28.22445}$	$\underline{28.22445}$
6	39.81565	$\underline{39.81550}$	$\underline{39.81550}$	$\underline{39.81550}$	$\underline{39.81550}$	$\underline{39.81550}$	$\underline{39.81550}$
7	53.24716	53.24670	53.24670	$\underline{53.24670}$	$\underline{53.24670}$	$\underline{53.24670}$	$\underline{53.24670}$
8	68.57598	68.57509	68.57509	68.57508	$\underline{68.54000}$	$\underline{68.54000}$	$\underline{68.54000}$
9	85.83486	85.83345	85.83344	85.83343	85.83346	85.83346	$\underline{85.80000}$
10	105.04398	105.04196	105.04196	105.04192	105.04197	105.04197	105.05767
11	126.21643	126.21373	126.21373	126.21367	126.21375	126.21375	126.22382
12	149.36107	149.35765	149.35765	149.35755	149.35767	149.35767	149.36685
13	174.48413	174.47994	174.47994	174.47981	174.47997	174.47997	174.48922
14	201.5901	201.58512	201.58511	201.58493	201.58515	201.58514	201.59482
15	230.68232	230.67651	230.6765	230.67626	230.67654	230.67653	230.68682
16	261.76329	261.75663	261.75662	261.75631	261.75667	261.75666	261.76765

The values of B_7 predicted by the three approximants are 53.2471596, 53.2467021 and 53.2467020, respectively. Since $[1/2]_B$ and $[2/1]_B$ are constrained by more virials, their results should be more reliable. Considering the uncertainty of predicted B_7 cannot be better than those of B_5 and B_6 used in the parameterization, the final result of B_7 is taken as 53.2467 in this work. The modified B_7 agrees with that simulated by Janse van Rensburg[14] (53.54 ± 0.29) and that carefully corrected by Kratky[21] (53.7 ± 0.8) within the uncertainties. The modified B_7 also agrees very well with the predicted value of the Pade approximants constrained by both simulated virials and highly accurate compressibility factors.[16] Recently, Kolafa *et al.*[11] obtained five values of B_7 from highly accurate EOS (53.08, 53.11, 53.33, 53.27, and 53.39). The average of the five values is 53.236, which is very close to our modified B_7.

The value of B_{10} can be refined using the known $B_3 - B_9$, where B_7 takes the refined value. Five approximants are used in this work. Their parameters are listed in Table 3, while the predicted values of $B_5 - B_{16}$ are given in Table 4.

As can be seen from Table 4, the B_{10} values predicted from the eight approximants agree very well with each other, and the maximum difference in B_{16} is only 0.01134. Considering the simulated uncertainties of $B_5 - B_9$ and the excellent consistency between the approximants used in this work, B_{10} can be taken as 105.042. This value is still in the uncertainty range of B_{10} [8,24] estimated by Labik *et al.*[7] It is also very close to the result (105) predicted from the highly accurate EOS of Erpenbeck and Wood.[13] Recently, Kolafa *et al.*[11] optimized five values of B_{10} (108, 108, 106, 106, 103) from accurate EOS, whose expectation is 106 ± 2.0.[7] This result agrees well with our modified value.

The high-order virials of $n \le 100$ predicted from the eight approximants are presented in Fig. 3. It is remarkable that the high-order virials predicted from the eight approximants agree very well with each other. The maximum relative deviations of predicted $B_5 - B_9$ are only 0.039% to 0.053%, which are obviously within or very close to the uncertainties of the most accurate simulated results. So far, none of the existing approaches can reach such good accuracy. The superiority of the present approaches is clearly shown in Figs. 1 and 3.

The results above strongly suggest that the approaches above can be safely extrapolated far beyond the order range of parameterization. Because of the lack of accurate high-order virials ($n > 10$), it is impossible to clearly determine the applicable range of order for each approximant. Nevertheless, the following facts are very useful for estimating the possible range of order: (1) The predominant contribution of order to B_n can be well described by n^2. (2) As n increases, $\Delta B_n/B_n$ decreases very rapidly, e.g., $\Delta B_{25}/B_{25} < 1\%$, $\Delta B_{50}/B_{50} < 0.27\%$. (3) The simulated values of $B_6 - B_{10}$ can be accurately reproduced by the simple approximants $[1/1]_B$, $[1/2]_B$ and $[2/1]_B$. (4) The predicted high-order virials from the eight approximants exhibit excellent consistency up to very high order ($n = 100$). This strongly suggests that ΔB_n can be accurately expressed by Pade-type functions up to very high order. With these facts, the highest valid order of the above approaches should be not lower than 30. Such a conservative upper limit of order is already much higher than those of the existing approaches, and is also enough for constructing a highly accurate virial EOS.

With the known $B_1 - B_{10}$ and the high-order virial coefficients ($n \ge 11$) predicted from the Pade-type approximants, the truncated virial equation can be improved systematically (Fig. 4). Apparently, the virial equation truncated at $n = 13$ is generally better than the well-known Carnahan-Starling (CS) equation[25] in the stable fluid region. When the order increases to 14, the truncated virial equation is much better than the CS equation in the whole stable fluid region, and only slightly worse than the CS equation in the metastable fluid region.

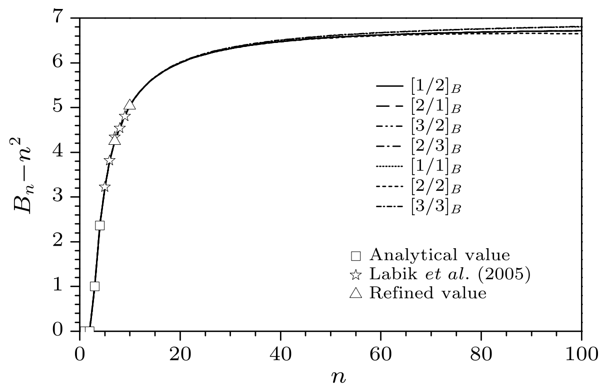

Fig. 3. Predicted $B_n - n^2$ ($n \le 100$) as a function of order n.

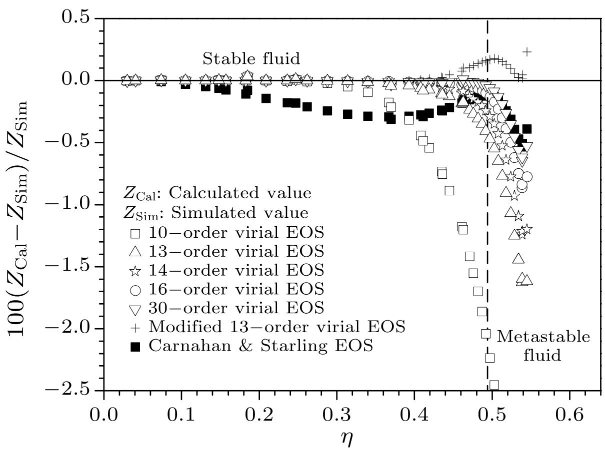

Fig. 4. Deviations of predicted compressibility factors. The simulated data are taken from Erpenbeck and Wood[13] and Kolafa *et al.*[11] The maximum deviation of the ten-order virial equation in the metastable region ($\eta \le 0.545$) is 5.0%, which is not shown in this figure.

We find that the contribution of higher-order terms not used in truncated virial EOS can be well approximated by adding a factor $(1 - c\eta)^{-1}$ to the last term ($c = 3\sqrt{2}/\pi$). With this modification, the truncated virial equations can be notably improved. For example, the virial equation truncated at $n = 13$ can be modified as

$$Z = 1 + \sum_{n=2}^{12} B_n \eta^{n-1} + \frac{B_{13}\eta^{12}}{1 - c\eta},\ (c = 3\sqrt{2}/\pi). \quad (4)$$

After this modification, the average and maximum deviations of predicted compressibility factors reduce from 0.060% and 0.41% to 0.024%, 0.16%, respectively (Fig. 4). By continuously using the following relation

$$\frac{\eta}{1 - c\eta} = \frac{1}{c}\Big(\frac{1}{1 - c\eta} - 1\Big). \quad (5)$$

Equation (4) can be rewritten as

$$Z = 1 + \sum_{n=1}^{11}\Big(B_{n+1} - \frac{B_{13}}{c^{12-n}}\Big)\eta^n + \frac{B_{13}}{c^{11}}\frac{\eta}{1 - c\eta}. \quad (6)$$

For the derivation of the fugacity coefficient, Eq. (6) is much more convenient than Eq. (4).

In conclusion, it is found that the first ten virial coefficients $B_1 - B_{10}$ can be reasonably approximated by n^2, and the remainders of virials B_n's ($n \ge 3$) can be expressed very accurately with Pade-type functions of n. Eight Pade-type approximants give very close results for the virials of $n \le 100$. This is a strong indication of the good reliability of the approximants. In analyzing the remainders of the n^2 approximation for the first ten virials, we find that the simulated B_7 and B_{10} are inconsistent with the other virials. According to the prediction of the approximants in this work, they are modified as 53.2467 and 105.042, respectively.

With the known and refined values of $B_2 - B_{10}$ and the predicted values of some higher-order virials, the compressibility factors of the hard-sphere system in the stable fluid region can be predicted very accurately, and those in the metastable fluid region can also be well predicted up to $\eta = 0.545$. The truncated virial EOS can be improved considerably by using the constraint of the close-packed limit.

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