High-order virial coefficients and equation of state for hard sphere and hard disk systems

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A very simple and accurate approach is proposed to predict the high-order virial coefficients of hard spheres and hard disks. In the approach, the nth virial coefficient B_n is expressed as the sum of n^{D-1} and a remainder, where D is the spatial dimension of the system. When $n \geq 3$, the remainders of the virials can be accurately expressed with Padé-type functions of n. The maximum deviations of predicted B_5–B_{10} for the two systems are only 0.0209%–0.0044% and 0.0390%–0.0525%, respectively, which are much better than the numerous existing approaches. The virial equation based on the predicted virials diverges when packing fraction $\eta = 1$. With the predicted virials, the compressibility factors of 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 $\eta = 0.545$. The compressibility factors of hard disk fluid can be predicted very accurately up to $\eta = 0.63$. The simulated B_7 and B_{10} for hard spheres are found to be inconsistent with the other known virials and therefore they are modified as 53.2467 and 105.042, respectively.

1. Introduction

Despite their simple intermolecular potentials, the hard sphere and hard disk systems exhibit a surprisingly rich structural and thermodynamic features of real systems.[1] For example, the hard sphere system can be present as stable fluid, metastable fluid,[2–4] solids (body-center or face-center cubic crystals),[3,5] glassy state,[6] and random close-packed state.[3,7,8] Similarly, the hard disk system also has several states, such as fluid, hexatic phase,[9] solid phase,[10,11] glassy state,[12] random jammed packing[7] or random close packing.[13] On the other hand, it is well accepted that the structural features of real systems are determined primarily by the repulsive intermolecular potential.[14] For these reasons, hard sphere and hard disk systems are commonly used as reference systems in the statistical mechanics[15] or macroscopic thermodynamics of more complicated model systems[16] and real systems.[17]

So far, many equations of state (EOS) have been proposed for hard spheres[2,18–30] and hard disks.[18,19,22,24,26,31–37] Among the numerous EOS, virial equation is the unique EOS that is exact in statistical mechanics (free of any *ad hoc* assumption), and can be systematically improved by adding higher order terms.[30,38,39] The virial equation is expressed as

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

where Z, P, V, T, R, η and B_n are the compressibility factor, pressure, molar volume, temperature, Avogadro constant, packing fraction and the nth virial coefficient reduced by the power of hard-core volume, respectively. For the hard sphere and hard disk systems, the first four virial coefficients (B_1–B_4) can be derived analytically,[40] *i.e.*

Hard sphere: $B_1 = 1$, $B_2 = 4$, $B_3 = 10$, $B_4 = 18.36476838\ldots$

Hard disk: $B_1 = 1$, $B_2 = 2$, $B_3 = 3.128017947\ldots$, $B_4 = 4.257854656\ldots$

The other virial coefficients need to be evaluated numerically, where the fifth to tenth virials have been determined using Monte Carlo simulations (Table 1).[19,31,38,41–48] Details on the research status of these virials can be found in a recent review made by Maters.[49] If only these virials are used to predict the compressibility factors of pure fluid in the isotropic region, *i.e.*, outside the fluid–solid transition region, the maximum deviation from the simulated results is over 2% for hard sphere system, and over 4% for hard disk system, which is *inadequate* for accurate theoretical or practical applications. Up to now, many approaches have been proposed to estimate the higher-order virials of hard spheres[2,19,22–26,28,30,31,35,39,42,44,47,48,50] and hard disks.[19,22,26,34–37,42,44,51,52] 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. Generally speaking, the accuracy or reliability of the predicted virials decreases rapidly as order increases. The commonly used Padé approximants often overestimate virials.[30] The Levin approximants are usually more accurate and reliable than Padé approximants, but they are not as convenient as Padé approximants. If we hope to extract high-order virials (*e.g.* $n > 10$) from simulated compressibility factors, it must be done with caution, because high-order virials are very sensitive to the deviations of compressibility factors. Kolafa *et al.*[28] and Kolafa and Rottner[36] offered good examples for this approach. In addition, there are also other problems in the prediction of high-order virials. One is the

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

	Hard sphere		Hard disk	
n	Labik *et al.*[47]	Clisby and McCoy[46,48]	Labik *et al.*[47]	Clisby and McCoy[46,48]
5	28.22445(10)	28.2245(3)	5.33689664(64)	5.33689664(16)
6	39.81550(36)	39.81515(93)	6.363026(11)	6.36296(13)
7	53.3413(16)	53.34442(37)	7.352080(28)	7.35186(28)
8	68.540(10)	68.538(18)	8.318668(62)	8.31910(44)
9	85.80(8)	85.813(85)	9.27236(29)	9.27214(90)
10		105.78(39)		10.2163(41)

singularity of the fluid–solid transition, which should accompany a local abrupt change in B_n in some range of order, and the second is the inconsistency among the known values of the first ten virials.

In order to obtain reliable high-order virials that are adequate for the construction of a highly accurate EOS for hard spheres and hard disks, it is very necessary to find better approaches. We found that there is a well-behaved relationship between the known virials and their orders, which can be used to develop very simple and accurate approaches for the prediction of high-order virials. We also correct the inconsistency among the ten known virials, and briefly discussed the limiting behavior of predicted virial coefficients.

2. Prediction of the high-order virial coefficients

2.1 General consideration

For hard spheres and hard disks, there is a well-behaved relationship between the known virials and their orders. We found that the known virials (B_1–B_{10}) can be roughly approximated by n^{D-1}, and each remainder is much smaller than n^{D-1}. For this reason, any nth virial coefficient can be expressed as

$$B_n = n^{D-1} + \Delta B_n \tag{2}$$

where ΔB_n is the remainder of n^{D-1} approximation. As can be seen from Fig. 1, $\Delta B_1 = \Delta B_2 = 0$, and the others behave as a function of n. For hard sphere system, ΔB_n is a monotonically increasing function of n, while for hard disk system it has a maximum value at $n = 6$. This is very different from $B_n - n$ curve.

Apparently, the simulated value of B_{10} for hard spheres is inconsistent with the overall trend of B_3–B_9. Furthermore, the value of B_7 for hard spheres is also slightly inconsistent with other virials. Since $\Delta B_n \ll n^{D-1}$, the inconsistency above is greatly weakened in $B_n - n$ 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 obviously larger than the uncertainties given by the original authors.[47,48] 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 hard sphere system (which has an unusual contribution to Z and B_n). However, if the singularity has 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

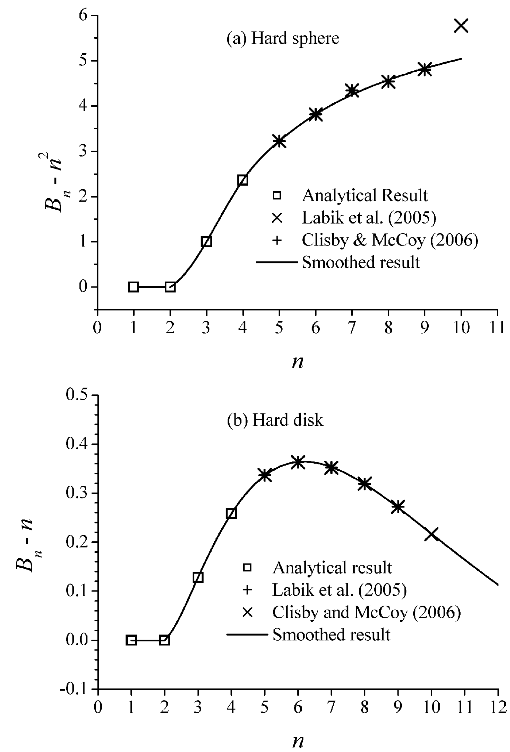

Fig. 1 The remainder $B_n - n^{D-1}$ as a function of n.

contribution. This is also supported by the ten known virials for hard disks (which do not exhibit any singularity). The following points also support the conclusions mentioned above. (1) The uncertainty in B_{10} is very likely underestimated. According to Labik *et al.*,[47] the expected error in B_{10} estimated by extrapolating the latest (and also the most accurate) values of B_5–B_9 is about ± 1, which is 2.56 times the uncertainty (± 0.39) reported by Clisby and McCoy.[46,48] In the estimated uncertainty range, the simulated value of B_{10} agrees well with other virials. (2) The uncertainty in B_7 has been underestimated many times in the past fifty years. This is evident in Table 2, where the lower limits of subsequently simulated values of B_7 often fall outside the uncertainty ranges of the older results. Therefore, it is not unexpected that the uncertainty in the latest B_7 was underestimated. Nevertheless, it should also be noted that the deviation of B_7 due to the inconsistency is still in the uncertainty ranges of some simulated results, such as those of Janse van Rensburg[42] (53.54 ± 0.29) and Kratky[45] (53.7 ± 0.8) (Table 2). The points above suggest that the inconsistency should come from the uncertainties of simulations, and thus should be corrected in a

Table 2 Simulated values of B_7 for hard sphere system

B_7	Lower limit	Upper limit	Reference	Year
56.5(1.6)	54.9	58.1	Ree and Hoover[31]	1967
56.1(2.5)	53.6	58.6	Kratky[44]	1977
53.7(8)	52.9	54.5	Kratky[45a]	1985
53.70(33)	53.37	54.03	Janse van Rensburg[41]	1993
53.54(29)	53.25	53.83	Janse van Rensburg[42]	1993
53.436(90)	53.346	53.526	Vlasov *et al.*[38]	2002
53.3444(37)	53.3407	53.3481	Clisby and McCoy[46]	2005
53.3413(16)	53.3397	53.3429	Labik *et al.*[47]	2005

[a] Corrected from the dependence of simulated result on the particle number of system

proper way. The details of the correction will be given in next section.

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 of the singular contribution at the present time. For convenience, we do not consider the singular contribution to B_n in this work. Thus 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 truncated virial equation.

We found that the known ΔB_n values of hard spheres and hard disks can be well formulated with Padé-type functions of order:

$$\Delta B_n = [L/M]_B = \Delta B_3 \frac{1+\sum_{l=1}^{L} b_l (n-3)^l}{1+\sum_{m=1}^{M} a_m (n-3)^m} \quad (n \geq 3) \qquad (3)$$

where $[L/M]_B$ denotes the approximant for B_n, which is completely different from the commonly used approximants for compressibility factor. For hard sphere system, $\Delta B_3 = 1$, so ΔB_3 can be omitted from the equation. In principle, an approximant like eqn (3) can be parameterized by $L + M$ virials ($n \geq 4$). This approach works very well for hard sphere system, but similar accuracy cannot be obtained for hard disk system. This is because the hard disk ΔB_n is a non-monotonic function of n, making the fitting more difficult. A better solution to this problem is the least-square fitting constrained by all the known virials. Before doing so, we noticed that B_3 and B_4 are derived from analytical expressions, so we force the approximant of interest to exactly reproduce ΔB_3 and ΔB_4, and then determine the other $L + M - 1$ parameters with B_5–B_{10}.

2.2 Prediction of virial coefficients

Since the uncertainties of virials simulated by Labik *et al.*[47] are obviously smaller than those of Clisby and McCoy,[48] we use the results of Labik *et al.*[47] to constrain the three approximants, but the value of B_7 for hard spheres used to parameterize $[2/2]_B$, $[2/3]_B$, $[3/2]_B$ and $[3/3]_B$ takes the result refined from $[2/1]_B$ and $[2/1]_B$. The details of the refinement are presented in next section. The parameters are given in Table 3–5.

As can be seen from Table 6 and 7, the known B_5–B_{10} are reproduced very accurately. The maximum deviations are

Table 3 Padé parameters for hard sphere system

$[L/M]_B$	$[1/1]_B$	$[1/2]_B$	$[2/1]_B$
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			$-0.3068293 \times 10^{-3}$
ΔB_∞	7.010571	0	$-\infty$

only 0.0390%–0.0525% and 0.0209%–0.0044%, respectively (Table 8). For hard sphere system, the deviations of all predicted values of B_6, B_8 and B_9 are within (or close to) the uncertainties of the simulated results. The predicted B_7 and B_{10} are also in excellent agreement with the overall trend of other known virials. This is unusual considering the parameterization of $[1/1]_B$, $[1/2]_B$ or $[2/1]_B$ for hard spheres only use B_4–B_5 or B_4–B_6.

The above approaches are compared in Fig. 2 with the existing approaches for hard spheres[2,19,22–26,28,31,35,39,42,44,47,48,50] and hard disks.[19,22,26,34–37,42,44,51,52] Many of the previous approaches show large deviations, only a few give accurate or reasonable results, such as those of Baram and Luban,[22] Erpenbeck and Wood,[23] Janse van Rensburg,[42] Speedy[2] and Kolafa *et al.*[28] for the hard sphere system, and those of Kratky,[34,44] Baram and Luban,[22] Janse van Rensburg,[42] Levin approximant[36] and Kolafa and Rottner[37] for the hard disk system.

2.3 Modification of B_7 and B_{10} for hard spheres

In order to predict B_7 and higher-order virials for hard sphere system, 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}. 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 than $[1/1]_B$, their results should be theoretically more reliable. On the other hand, the uncertainty of predicted B_7 cannot be better than those of B_5 and B_6 used in the parameterization (± 0.00010 and ± 0.00036), and thus we take 53.2467 as the best estimate of B_7. This modified B_7 agrees with the simulated value of Janse van Rensburg[42] (53.54 $\pm$ 0.29) and the result of Kratky[45] obtained from finiteness correction (53.7 $\pm$ 0.8) within the uncertainties. It is very interesting that every new value of B_7 is always lower than the previous ones, as can be seen in Table 2. Our modification is consistent with this decreasing trend.

Recently, Kolafa *et al.*[28] 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 value 53.2467. The doubly constrained Padé approximants of Speedy[2] also support our modification. He allowed the simulated B_6–B_8 to vary within $\pm 1.5E_k$ (where E_k is the uncertainty of B_k) and then optimized the Padé-type EOS in the fluid region up to $\eta/\eta_{cp} = 0.50$ (η_{cp} is the closest packing fraction). The Padé approximants obtained in this way should be much more reliable than those without considering the uncertainties of known virials and/or the constraints of highly accurate compressibility factors. The optimized B_7–B_{10} are 53.13, 68.57, 86.5 $\pm$ 0.7

Table 4 Padé parameters for hard sphere system

$[L/M]_B$	$[2/2]_B$	$[2/3]_B$	$[3/2]_B$	$[3/3]_B$
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}
ΔB_∞	7.247986	0	∞	7.014953

Table 5 Padé parameters for hard disk system

$[L/M]_B$	$[2/2]_B$	$[3/2]_B$	$[4/2]_B$	$[4/3]_B$
a_1	0.1618191×10^{-1}	$0.2328215 \times 10^{+0}$	$-0.6217322 \times 10^{-1}$	$-0.4557538 \times 10^{-2}$
a_2	0.2496862×10^{-1}	0.9204850×10^{-1}	0.5663712×10^{-1}	0.5024220×10^{-1}
a_3				$-0.1001683 \times 10^{-1}$
b_1	$0.1209296 \times 10^{+1}$	$0.1320411 \times 10^{+1}$	$0.1092781 \times 10^{+1}$	$0.1113382 \times 10^{+1}$
b_2	$-0.1122036 \times 10^{+0}$	$0.3999558 \times 10^{+0}$	$-0.1136275 \times 10^{+0}$	0.2963938×10^{-1}
b_3		$-0.5180408 \times 10^{-1}$	0.2664155×10^{-1}	$-0.6148428 \times 10^{-1}$
b_4			$-0.2738986 \times 10^{-2}$	0.4511989×10^{-2}
ΔB_∞	−4.49378546	$-\infty$	$-\infty$	∞

Table 6 Predicted B_5–B_{18} for hard sphere system. Bold values are the 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	**28.22445**	**28.22445**	**28.22445**	**28.22445**	**28.22445**	**28.22445**	**28.22445**
6	39.81565	**39.81550**	**39.81550**	**39.81550**	**39.81550**	**39.81550**	**39.81550**
7	53.24716	53.24670	53.24670	**53.24670**	**53.24670**	**53.24670**	**53.24670**
8	68.57598	68.57509	68.57509	68.57508	**68.54000**	**68.54000**	**68.54000**
9	85.83486	85.83345	85.83344	85.83343	85.83346	85.83346	**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
17	294.83495	294.82743	294.82741	294.82703	294.82747	294.82745	294.83923
18	329.89883	329.89042	329.89040	329.88993	329.89046	329.89045	329.90304

Table 7 Predicted B_5–B_{18} for hard disk system. Bold values are known virials

n	$[2/2]_B$	$[3/2]_B$	$[4/2]_B$	$[4/3]_B$
5	5.3357817	5.3369121	5.3368695	**5.3368966**
6	6.3637709	6.3628478	6.3631096	**6.3630260**
7	7.3533877	7.3522113	7.3519594	**7.3520800**
8	8.3184366	8.3189594	8.3187611	**8.3186680**
9	9.2704366	9.2719487	9.2723221	**9.2723600**
10	10.2173373	10.2164417	10.2163064	10.2163000
11	11.1639666	11.1555572	11.1517235	11.1610862
12	12.1129488	12.0911779	12.0784803	12.1012156
13	13.0655227	13.0244698	12.9961172	13.0401543
14	14.0221215	13.9561740	13.9041107	13.9785115
15	14.9827401	14.8867743	14.8019827	14.9166391
16	15.9471535	15.8165932	15.6893295	15.8547401
17	16.9150418	16.7458510	16.5658217	16.7929306
18	17.8860571	17.6747007	17.4311937	17.7312741

and 106.7 ± 1.0, respectively. These values agree very well with the latest simulated results, where B_7 (53.13) is slightly smaller than our modified value. Besides, the modified B_7 also agrees with the predicted value of Levin approximation (54.1 ± 1.6).[22]

The value of B_{10} can be refined on the basis of the known B_3–B_9, where B_7 takes the refined value. Five more approximants are used here. Their parameters are listed in Table 4. Now, there are totally eight Padé approximants for the hard sphere system.

As can be seen in Table 6, the B_{10} values predicted from the eight approximants agree very well with each other, where the maximum difference in B_{10} is less than 0.016. Considering the simulated uncertainties of B_5–B_9 and the excellent consistency between our approximants, B_{10} can be taken as 105.042. This value is very close to the result (105) predicted from the highly accurate EOS of Erpenbeck and Wood.[23] Recently, Kolafa *et al.*[28] optimized five values of B_{10} from accurate EOS (108, 108, 106, 106, 103), whose statistical expectation is 106 ± 2.0.[47] This result agrees well our modified value. According to the Padé approximant constrained by the latest virials,[47] B_{10} = 106.5. The Padé approximants of Speedy[2] constrained by both known virials and simulated compressibility factors also predict a very close result (106.7 ± 1.0). These results are not unexpected considering Padé approximants almost always overestimate high-order virials not used in parameterization.

Table 8 Deviations (%) of predicted virial coefficients

N		5	6	7	8	9	10
Hard sphere	$[1/1]_B$	^{a}	0.0004	0.0009	0.0525	0.0406	^{b}
	$[1/2]_B$, $[2/1]_B$	^{a}	^{a}	^{b}	0.0512	0.0390	^{b}
	$[2/2]_B$	^{a}	^{a}	^{b}	0.0512	0.0390	^{b}
	$[2/3]_B$, $[3/2]_B$	^{a}	^{a}	^{b}		0.0390	^{b}
Hard disk	$[2/2]_B$	−0.0209	0.0117	0.0178	−0.0028	−0.0207	0.0102
	$[3/2]_B$	0.0003	−0.0028	0.0018	0.0035	−0.0044	0.0014
	$[4/2]_B$	−0.0005	0.0013	−0.0016	0.0011	−0.0004	0.0001

^{a} The corresponding virial coefficient is used in the parameterization of Padé approximant, so it is reproduced exactly. ^{b} The deviation is not calculated, because the value of B_n has been modified.

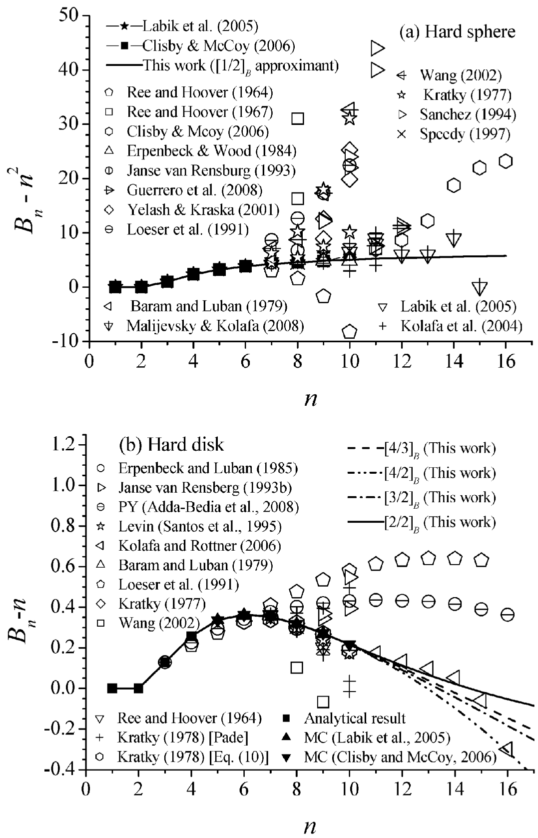

Fig. 2 Comparison of the remainders from different approaches with the computer simulation data. Solid and opened symbols denote the simulated (or analytical) values and predicted values, respectively. The estimated values are only given for $n \geq 7$. The PY results for hard disks are weighted average of the PY solutions for compressibility and pressure approximations,[52] where the compressibility result takes a weight of 0.74384 used by Kratky.[34]

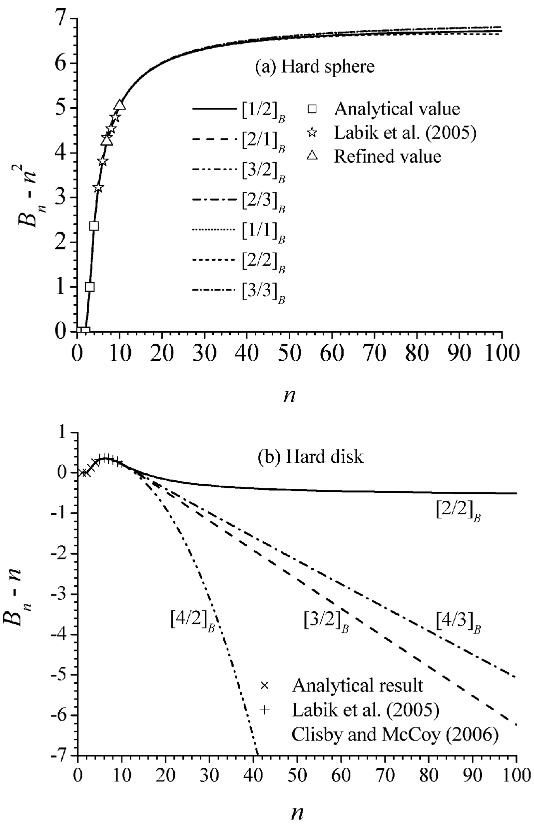

Fig. 3 Predicted $B_n - n^{D-1}$ ($n \leq 100$) as a function of order n.

2.4 The reliability of extrapolated virial coefficients

The predicted values of B_n ($n \leq 100$) are presented in Fig. 3. The high-order virials for hard sphere system predicted from the eight approximants are in excellent agreement with each other. The difference in B_{100} is less than 0.161. The above results strongly suggest that the approximants for hard sphere system 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 latest values of B_{11}–B_{15} (130 ± 2, 150 ± 5, 175 ± 7, 205 ± 10, 225 ± 25) estimated by Malijevsky and Kolafa[50] from optimized differential approximants can serve as a preliminary test, where the uncertainties were estimated from the known virials and simulated compressibility factors. The predicted values of B_{11}–B_{15} in Table 6 are mostly within the uncertainty ranges. The only exception is B_{11}, which is slightly smaller than the lower limit of the estimated value. This is not unexpected, because the certainty estimation of Malijevsky and Kolafa[50] used the simulated results of Clisby and McCoy,[46,48] where the uncertainty in B_{10} was notably underestimated.[47]

In addition to the above results, 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^{D-1}.

(2) As n increases, the ratio $\Delta B_n/B_n$ 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 reproduced very accurately by the simple approximants $[1/1]_B$, $[1/2]_B$ and $[2/1]_B$, although their parameterization only uses B_3–B_5 or B_3–B_6.

(4) The predicted high-order virials from the eight approximants exhibit excellent consistency up to very high order ($n = 100$). Combined with the excellent performance of $[1/1]_B$, $[1/2]_B$ and $[2/1]_B$ in the prediction of B_7–B_{10}, this consistency can be regarded as an indication that ΔB_n can be accurately expressed by Padé-type functions of up to very high order.

With the facts above, a conservative estimate of the applicable order of the above approaches should be not lower than $n = 20$. Such an upper limit of order is already much higher than those of the existing approaches, and also enough for constructing a highly accurate EOS.

Different from the approximants for hard spheres, good agreement between the four approximants for hard disks only exists up to B_{15}–B_{20}. At higher orders, the approximants differ obviously from each other. So far, no reliable high-order virials can be used to determine the overall trend of hard disk virials at $n > 10$. The best high-order virials may be the results for B_{11}–B_{16} obtained by Kolafa and Rottner[37] from accurate EOS, whose uncertainties are 0.010, 0.03, 0.06, 0.08, 0.21 and 0.4, respectively. The large uncertainties of B_{15} and B_{16} should closely relate to the obvious inconsistency between B_{15}–B_{16} and B_{11}–B_{14} (Fig. 2). This is not unexpected, because higher order virials are more sensitive to the deviations of EOS than the lower order virials. Besides, the good performance of the EOS[37] in the fluid–solid transition region indicates that the fitted values of B_{15} and B_{16} are likely to be affected by the singularity in the phase transition region (which has a negative contribution to fitted B_n). Nevertheless, it is interesting that the predicted B_{11}–B_{16} from $[2/2]_B$ are all in the uncertainty ranges of B_{11}–B_{16} reported by Kolafa and Rottner.[37] The predicted B_{11}–B_{16} from $[4/3]_B$ are mostly in the uncertainty ranges, where only B_{11} and B_{12} are exceptional, but they are only slightly (0.001) smaller than the lower limits of B_{11} and B_{12} obtained by Kolafa and Rottner.[37] According to the results in Fig. 2, $[4/2]_B$ should be the worst of the four approximants. If no singularity occurs before $n = 20$, the other three approximants should be valid up to $n = 15$ or higher order, and one or two of them (such as $[2/2]_B$) should be valid up to much higher order.

3. The limiting behavior of predicted virial coefficients

The parameters in Table 3–5 can be used to analyze the limiting behaviors of the approximants. As n tends to infinite, the approximants show three kinds of limiting behavior: if $L > M$, the approximant will be divergent; if $L < M$, it will converge to zero; and if $L = M$, it will converge to a constant. It is interesting that the limits of the three symmetrical approximants ($[1/1]_B$, $[2/2]_B$ and $[3/3]_B$) for the hard sphere system are only slightly different. As expected, very close results for ΔB_n can be obtained from the three symmetrical approximants in the full range of order. The $[1/2]_B$ and $[2/3]_B$ (or $[2/1]_B$ and $[3/2]_B$) approximants for hard sphere system also have very close results.

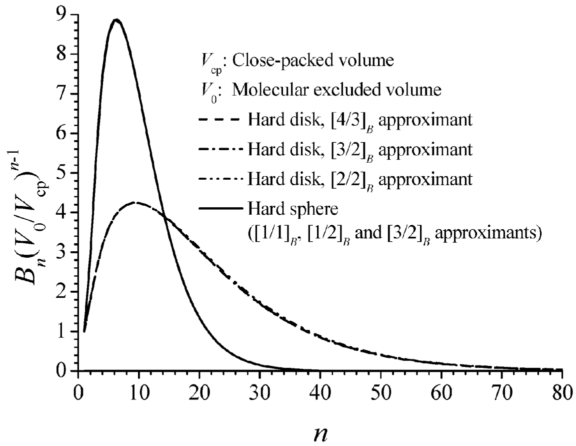

Fig. 4 Virial coefficients reduced by the powers of relative volume V_{cp}/V_0.

Despite the great difference in the limiting behavior of ΔB_n, all approximants for hard spheres and hard disks have the same limiting behavior in Fig. 4 and 5:

$$\lim_{n\to\infty} B_n \left(\frac{V_0}{V_{cp}}\right)^{n-1} = \lim_{n\to\infty} B_n \eta_{cp}^{n-1} = 0 \quad (4)$$

$$\lim_{n\to\infty} \frac{B_n}{B_{n-1}} = 1 \quad (5)$$

where V_0 is the molar volume of hard sphere molecules, and V_{cp} is the molar volume of the hard sphere system in the close packed limit. The limit in eqn (4) is consistent with those of the dimensional interpolation of D-dimensional virials.[35] Furthermore, the first 40 values of $B_n(V_0/V_{cp})^{n-1}$ from dimensional interpolation of virials[35] also agree well with those predicted from the above approximants. Eqn (5) is the same as the exact Percus–Yevick solution for hard sphere system.[53] The virials calculated from the Carnahan–Starling (CS) equation[20] also give the same limiting result.

Eqn (5) is a very important property since it suggests that if m is sufficiently large, the ratio of the $(m + 1)$th and mth terms in the virial equation will be very close to η, *i.e.*

$$q = \frac{B_{m+1}\eta^m}{B_m \eta^{m-1}} = \frac{B_{m+1}}{B_m}\eta \approx \eta \quad (6)$$

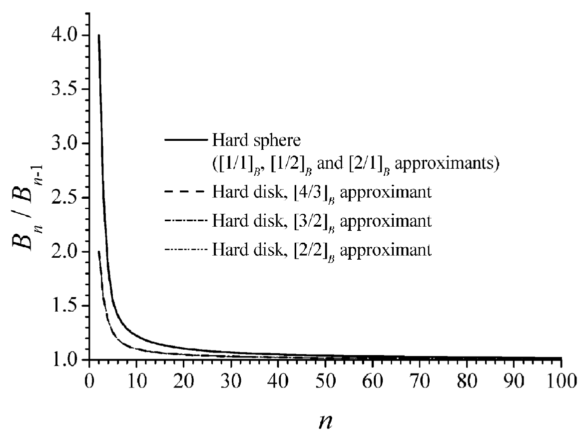

Fig. 5 Ratios of virial coefficients.

In other words, the higher-order terms after the mth term in the virial equation can be well approximated by an infinite geometric sequence with a common ratio $q = \eta$. By summating the sequence, one can obtain a good approximation for the contribution of the higher-order terms to Z. In this way, we have

$$Z \approx \sum_{n=1}^{m} B_n \eta^{n-1} + \frac{B_{m+1}\eta^m}{1-\eta} \tag{7}$$

where the first term is the contribution of the virial equation truncated at the mth term. Eqn (7) clearly shows that the virial expansion for hard sphere or hard disk system has a pole at $\eta = 1$. This pole determines the radii of convergence of the EOS for the systems. It also confirms the theoretical derivation of Yelash *et al.*:[29] the limit of the ratio B_n/B_{n+1} (or B_n/B_{n-1}) is equal to the packing fraction at the pole of an EOS. Therefore, the virial equation cannot predict the existence of fluid to solid transition. This is consistent with the results of Percus–Yevick solutions of hard sphere and hard disk systems.

As expected, the deviation of eqn (7) from exact Z increases as m decreases. If m is not large enough, the common ratio q must be modified as $q = c\eta$ ($c > 1$) so that the contribution of high-order terms after the mth term can be fitted as accurate as possible. In these cases, Z can be approximated as

$$Z \approx \sum_{n=1}^{m} B_n \eta^{n-1} + \frac{B_{m+1}\eta^m}{1-c\eta} \tag{8}$$

According to the results shown in Fig. 5, the constant c in eqn (8) must be in the range of $1 \le c \le 4$. Apparently, eqn (8) degenerates into eqn (7) when $c = 1$. For many practical applications, $m = 15$–20 would be adequate if c is properly chosen.

4. Prediction of compressibility factors

In order to obtain a reliable assessment of truncated forms of virial equation, we need highly accurate compressibility factors. In the past decades, molecular dynamics and Monte Carlo simulations have obtained extensive data for the compressibility factors of hard spheres[23,27,28,54,55] and hard disks,[11,37,51,55,56] and most of them are consistent with each other. Based on the consideration of accuracy and consistency, we use the data of Erpenbeck and Wood,[23] Erpenbeck and Luban,[51] Kolafa *et al.*[28] and Kolafa and Rottner.[37]

As shown in Fig. 6, truncated virial EOS can be improved systematically by adding more terms. For the hard disk system, the virial EOS truncated at $n = 13$ is already obviously better than the Henderson equation[33] in the fluid region $\eta \le 0.71$. For hard sphere system, the virial EOS truncated at $n = 14$ is already much better than the CS equation in the whole stable fluid region ($\eta \le 0.497$). In the metastable fluid region, it is only slightly worse than the CS equation. If the virial equation is truncated at higher order, it will be much more accurate.

The discussion in last section suggests that the contribution of higher-order terms not used in the truncated virial equation can be approximately described by adding a simple factor $(1 - c\eta)^{-1}$ ($c \ge 1$) to the last term. The resulting EOS is has

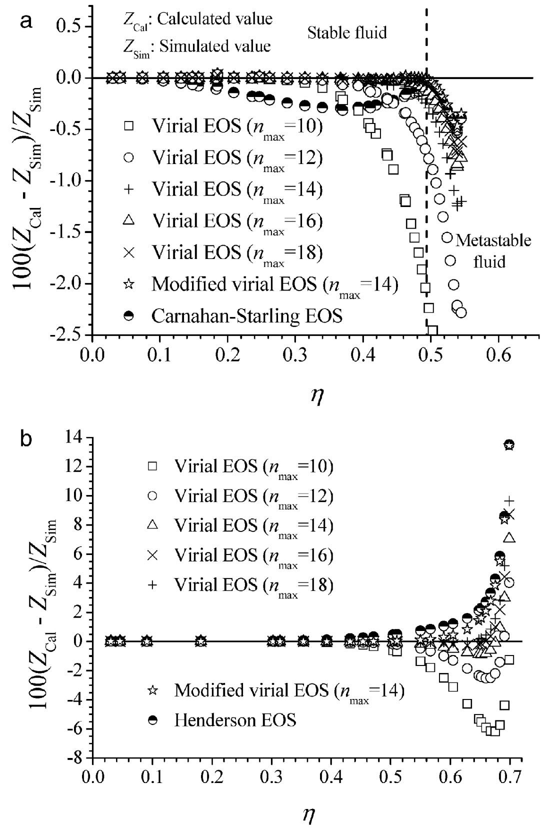

Fig. 6 Deviations of predicted compressibility factors from those of molecular simulations. (a) Hard sphere $[3/3]_B$ and (b) hard disk $[4/3]_B$. n_{max} is the maximum order of virial coefficients in the truncated virial equation. The maximum deviation of the tenth virial equation for hard sphere system in the metastable region ($\eta \le 0.545$) is 5.0%, which is not shown.

the form of eqn (8). By continuous use of the following relation

$$\frac{\eta}{1-c\eta} = \frac{1}{c}\left(\frac{1}{1-c\eta} - 1\right) \tag{9}$$

Eqn (8) can be rewritten as

$$Z = 1 + \sum_{n=1}^{m-1}\left(B_{n+1} - \frac{B_{m+1}}{c^{m-n}}\right)\eta^n + \frac{B_{m+1}}{c^{m-1}}\frac{\eta}{1-c\eta} \tag{10}$$

This form is very convenient for the derivation of fugacity coefficient. In addition to eqn (8), we also test the following modification:

$$Z = 1 + \frac{B_2\eta}{1-c\eta} + \sum_{n=3}^{m}(B_n - B_2c^{n-2})\eta^{n-1} \quad (c \ge 1) \tag{11}$$

Table 9 summarizes the deviations of several truncated virial equations and their modified forms. Generally, the two modifications above are better than their corresponding truncated virial equations, but the improvement becomes weaker and weaker as the order of the equation increases. However, we should notice the following facts: (i) eqn (11) for hard spheres with $c = 1/\eta_{cp}$ only has marginal improvement. (ii) There are also exceptional cases. For example, the performance of eqn (8) for hard disks with $c = 1/\eta_{cp}$ is worse

Table 9 Deviations (%) of truncated virial equations and their modified versions for hard spheres (upper part) and hard disks (lower part). AD and MD are the average and maximum deviations of predicted compressibility factors, respectively. η_{cp} is the closest packing fraction. The calculated density range of the hard sphere fluid is $\eta \leq 0.497$, and that of the hard disk fluid is $\eta \leq 0.63$

			Eqn (8)				Eqn (11)			
	Truncated virial equation		$c = 1$		$c = 1/\eta_{cp}$		$c = 1$		$c = 1/\eta_{cp}$	
Order	AD	MD	AD	MD	AD	MD	AD	MD	AD	MD
				Hard spheres						
10	0.3575	2.0403	0.1078	0.6428	0.1284	0.8179	0.1539	0.8364	0.3480	1.9871
12	0.1076	0.6910	0.0322	0.2097	0.0430	0.2934	0.0282	0.1591	0.1056	0.6782
14	0.0352	0.2431	0.0132	0.0858	0.0139	0.0787	0.0056	0.0324	0.0348	0.2400
16	0.0147	0.1006	0.0087	0.0511	0.0059	0.0324	0.0061	0.0324	0.0146	0.0999
18	0.0092	0.0567	0.0077	0.0416	0.0063	0.0324	0.0092	0.0565	0.0055	0.0324
				Hard disks						
10	0.1033	4.2637	0.0182	0.7382	0.0071	0.4400	0.0866	3.5736	0.0562	2.2514
12	0.0402	1.8569	0.0058	0.2083	0.0049	0.3427	0.0345	1.5845	0.0206	0.8910
14	0.0154	0.7519	0.0015	0.0501	0.0032	0.2512	0.0134	0.6443	0.0070	0.2882
16	0.0056	0.2546	0.0011	0.0821	0.0022	0.1946	0.0049	0.2121	0.0020	0.0679
18	0.0018	0.0606	0.0014	0.1145	0.0019	0.1642	0.0015	0.0516	0.0012	0.0727

than their corresponding truncated virial equation when the order increases to 18. This can be explained by the difference in the nature of the fluid–solid transitions of the hard sphere and hard disk systems. Now, it has been determined that the fluid–solid transition in hard disk system consists of two separate stages: the transition from isotropic fluid to hexatic phase, and that from hexatic phase to solid phase, where the first stage is a second-order transition.[9,57] This is very different from the first-order fluid–solid transition in hard sphere system. It is well known that the experimental compressibility factors of real fluids near the gas–liquid critical point (a second-order transition) are always lower than those predicted from the classical EOS parameterized with the thermodynamic data outside the critical region. This suggests that the critical singularity has a negative contribution to Z. So is the fluid–solid transition in hard disk system. When the virial equation for hard disks is truncated at $n = 18$, the equation is already very accurate. If the $1/\eta_{cp}$ factor is added to the equation, the predicted Z will inevitably be overestimated. Different from the hard disks, the modification in eqn (8) for hard spheres is always better than its corresponding truncated virial EOS. This is because the metastability of the hard sphere system in the fluid–solid transition region has a positive contribution to Z, which is qualitatively consistent with the contribution of the $(1 - c\eta)^{-1}$ factor.

5. Conclusions

It is found that the known virial coefficients B_n ($n = 1$–10) for hard spheres and hard disks can be reasonably approximated by n^{D-1}, and the remainders of B_ns ($n \geq 3$) can be expressed very accurately with Padé-type functions of n. Eight Padé-type approximants for hard spheres give very close results for $n \leq 100$. This is a strong indication of the good accuracy and reliability of the approximants. In the study of the remainders, we found the simulated B_7 and B_{10} for hard spheres are inconsistent with the other known virials. According to the prediction of the approximants in this work, they are modified as 53.2467 and 105.042, respectively. Unlike the monotonically increasing remainders for hard spheres, the known remainders for hard disks show maximum at $n = 6$. This nature increases the difficulty in the prediction of higher-order virials. The corresponding Padé-type approximants for this system differ obviously from each other when $n > 20$.

By analyzing the limiting behavior of the predicted virials, we found that the viral equations for both hard spheres and hard disks have a pole at the inaccessible packing fraction $\eta = 1$. The truncated virial equations based on the known and refined values of B_2–B_{10} and the predicted values of some higher-order virials are adequate for accurate prediction of hard sphere compressibility factors in the whole stable fluid region, and those in the metastable fluid region can also be well predicted up to $\eta = 0.545$. The truncated high-order virial EOS can be improved considerably by introducing a repulsive factor $(1 - \eta_{cp})^{-1}$. The hard disk system also has similar results for most of the fluid region ($\eta \leq 0.63$). The exception only appears in the vicinity of the fluid–solid transition point.

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