ARTICLE

Improvement on the Carnahan-Starling Equation of State for Hard-sphere Fluids

Xian-zhi Wang*, Hong-ru Ma

Institute for Theoretical Physics, Department of Physics, Shanghai Jiao Tong University, Shanghai 200240, China

(Dated: Received on September 12, 2010; Accepted on November 3, 2010)

Making use of Weierstrass's theorem and Chebyshev's theorem and referring to the equations of state of the scaled-particle theory and the Percus-Yevick integration equation, we demonstrate that there exists a sequence of polynomials such that the equation of state is given by the limit of the sequence of polynomials. The polynomials of the best approximation from the third order up to the eighth order are obtained so that the Carnahan-Starling equation can be improved successively. The resulting equations of state are in good agreement with the simulation results on the stable fluid branch and on the metastable fluid branch.

Key words: Hard-sphere fluid, Virial coefficient, Carnahan-Starling equation of state

I. INTRODUCTION

As is well known, the intermolecular potential plays a decisive role for the occurrence of phase transitions [1]. The attractive part of the intermolecular potential is necessary for the occurrence of the gas-liquid phase transition while the short range repulsive part is responsible for the occurrence of the liquid-solid phase transition. The simplest models exhibiting the fluid-solid phase transition are the hard-sphere models which have merely excluded volume interactions [2–11]. At sufficiently low temperatures quantum effect is not negligible [12]. Researchers have found experimentally that the behaviors of colloidal spheres coated with poly-12-hydroxystearic acid are very close to the hard-sphere interactions [13]. Hence nowadays we no longer regard hard-sphere models as artificial models. There exists a long history for the studies of hard-sphere models. As early as in 1936, Tonks obtained an exact solution of one-dimensional hard-sphere models [2]. Unfortunately, no exact solution exists for higher dimensions. Researchers have used analytical, numerical, and experimental methods to study the models.

Since the reference systems in the perturbation theory are usually taken to be hard-sphere systems [6], accurate equations of state for hard-sphere models are needed as inputs. Many analytical and empirical equations of state have been proposed [6, 7, 10, 11, 14, 15]. For hard-disk fluids, Wang has proposed a simple and accurate equation of state [16]

$$\frac{P}{\rho k_\mathrm{B}T} = \frac{1+0.128y^2-0.06y^4-0.11y^6}{(1-y)^2} \qquad (1)$$

$$y = \frac{\pi a^2\rho}{4} \qquad (2)$$

where P is the pressure, ρ the number density, T the absolute temperature, k_B the Boltzmann constant, , and a is the diameter of the hard disk. The virial coefficients predicted by this equation are in good agreement with the exact ones, with errors less than 0.5%. In the density range $0<\rho a^2\leq 0.83$, the predicted pressures are in good agreement with the simulation results. For $0<\rho a^2\leq 0.70$, the errors are less than 0.007%. Even at $\rho a^2=0.83$, the error is only 0.5%.

Of the proposed equations of state for three-dimensional hard-sphere fluids, some are simple but inaccurate and some are accurate but complicated [6, 7, 10, 11, 14, 15]. The Carnahan-Starling (CS) equation is the only one that is both simple and accurate [17]. The virial coefficients predicted by this equation were in good agreement with the exact ones obtained before 2005. The pressures predicted by this equation were in good agreement with the simulation results obtained before 2010 [3, 18, 19]. Hence this equation had found wide applications in the studies of liquids. Nevertheless, very accurate numerical results have been obtained in recent years [14, 20, 21]. It was found that the CS equation is not very accurate. The CS equation needs to be improved. In this work, we will show that the CS equation is not a lone result and can be improved successively.

*Author to whom correspondence should be addressed. E-mail: xzwang@sjtu.edu.cn

II. BASIC APPROACH

For a hard-sphere fluid, the virial expansion is

$$\frac{P}{\rho k_{\rm B}T} = 1+\sum_{n=1}^{\infty} B_{n+1}\rho^n = 1+\sum_{n=1}^{\infty} B'_{n+1}(B_2\rho)^n = 1+\sum_{n=1}^{\infty} B^*_{n+1}y^n \quad (3)$$

where B_n is the nth virial coefficient, B'_{n+1}=B_{n+1}/B_2^n, B^*_{n+1}=$4^nB'_{n+1}$, B_2=$2\pi a^3/3$, y=$\pi a^3\rho/6$=$B_2\rho/4$, and a is the diameter of the hard sphere.

The scaled-particle theory [22, 23] gives

$$\frac{P}{\rho k_{\rm B}T} = \frac{1+y+y^2}{(1-y)^3} \quad (4)$$

The Percus-Yevick integration equation for a hard sphere fluid admits an exact solution [24, 25]. Two equations of states obtained from compressibility equation and from virial equation are

$$\frac{Pv}{k_{\rm B}T} = \frac{1+y+y^2}{(1-y)^3} \quad (5)$$

$$\frac{Pv}{k_{\rm B}T} = \frac{1+2y+3y^2}{(1-y)^2} \quad (6)$$

Taking a (2/3:1/3) average of the compressibility pressure Eq.(5) and the virial pressure Eq.(6), Carnahan and Starling obtained a simple and accurate equation of state [17]

$$\frac{P}{\rho k_{\rm B}T} = \frac{1+y+y^2-y^3}{(1-y)^3} \quad (7)$$

$$B^*_n = (n-1)(n+2), \quad n\geq 2 \quad (8)$$

Recently, Labik *et al.* have numerically calculated the virial coefficients up to B_9 [20]. Clisby and McCoy have numerically calculated the virial coefficients up to B_{10} [21]. The numerical results obtained by the two groups are very close to each other. Here we use the results of Clisby and McCoy: B'_2=1, B'_3=0.625, B'_4=0.2869495$\cdots$, B'_5=0.110252(1), B'_6=0.03888198(91), B'_7=0.01302354(91), B'_8= 0.0041832(1), B'_9=0.0013094(13), B'_{10}=0.0004035(15). These results can be expressed as a formula

$$B^*_n = (n-1)(n+2)+\epsilon_n, \quad 2\leq n\leq 10 \quad (9)$$

with ϵ_2=ϵ_3=0, ϵ_4=0.3648, ϵ_5=0.2245, ϵ_6=−0.1849, ϵ_7=−0.6556, ϵ_8=−1.4625, ϵ_9=−2.1872, ϵ_{10}=−2.225, where ϵ_n represents the deviation from the predictions of the CS equation and is a monotonically decreasing function of n for n≥4. We see that ϵ_n is a regular function of n, which indicates that successive improvements on CS equation are possible.

Using these known virial coefficients, we obtain the Padé approximations [4/5] and [5/4]

$$\frac{P}{\rho k_{\rm B}T} = (1+1.97909y+3.24059y^2+2.19327y^3+ 0.83631y^4)/(1-2.02091y+1.32424y^2- 1.25934y^3+1.52049y^4-0.583676y^5) \quad (10)$$

$$\frac{P}{\rho k_{\rm B}T} = (1+3.20154y+7.52283y^2+9.20259y^3+ 7.7996y^4+2.99407y^5)/(1-0.798462y+ 0.716679y^2-4.04431y^3+3.24915y^4) \quad (11)$$

For hard-sphere fluids, both the equations of state of the scaled-particle theory and the Percus-Yevick integration equation suggest that the equation of state should have the functional form

$$\frac{P}{\rho k_{\rm B}T} = \frac{f(y)}{(1-y)^3} \quad (12)$$

where $f(y)$ is a function to be determined.

Let us use Weierstrass's theorem to get $f(y)$ [16, 26]. Weierstrass's theorem [27] states that if $f(x)$ is continuous on the closed interval $[a,b]$, there exists a sequence of polynomials $H_n(x)$ such that

$$\lim_{n\to\infty} H_n(x) = f(x) \quad (13)$$

$$H_n(x) = \sum_{j=0}^{n} a_{nj}x^j \quad (14)$$

This theorem tells us that there exists a set of coefficients a_{nj}, n=0, $\cdots$, ∞, j=0, $\cdots$, n, such that $\sum_{j=0}^{n} a_{nj}x^j$ tends uniformly to $f(x)$ as $n\to\infty$.

According to Chebyshev's theorem [27], there exists a unique polynomial of the best approximation for the set $H_n(x)$ ($n\leq m$).

Since the pressure is a continuous function of density in the whole fluid regime, so $P(1-y)^3/\rho k_{\rm B}T$=$f(y)$=$f(\pi a^3\rho/6)$ is a continuous function of density in the whole fluid regime [16]. So $P(1-y)^3/\rho k_{\rm B}T$=$f(y)$ is continuous on the closed interval $[0, \pi a^3\rho_f/6]$. There exists a sequence of polynomials $H_n(y)$ such that

$$\lim_{n\to\infty} H_n(y) = f(y) = \frac{P(1-y)^3}{\rho k_{\rm B}T}, \quad 0\leq y\leq \frac{\pi a^3\rho_f}{6} \quad (15)$$

where $H_n(y)$=$1+a_{n1}y+a_{n2}y^2+\cdots+a_{nn}y^n$ is a polynomial of order n in y and ρ_f is the freezing density. The polynomial of the best approximation can be obtained as follows. Choose the values of the coefficients of the polynomial and calculate the resulting virial coefficients and pressures. Compare the calculated results with the known numerical results and obtain the errors.

DOI:10.1088/1674-0068/23/06/675-679

TABLE I The virial coefficients B_n^* for a hard-sphere fluid.

B_n^*	Exact	$\mathcal{H}_3$	$\mathcal{H}_4$	$\mathcal{H}_5$	$\mathcal{H}_6$	$\mathcal{H}_7$	$\mathcal{H}_8$	[5/4]
B_2^*	4	4	4	4	4	4	4	4
B_3^*	10	10	10	10	10	10	10	10
B_4^*	18.3648	18	18.3648	18.3648	18.3648	18.3648	18.3648	18.3648
B_5^*	28.2245	28	28.3944	28.2245	28.2245	28.2245	28.2245	28.2245
B_6^*	39.8151	40	40.0888	39.9161	39.8151	39.8151	39.8151	39.8151
B_7^*	53.3444	54	53.448	53.4396	53.3066	53.3444	53.3444	53.3444
B_8^*	68.5375	70	68.472	68.795	68.699	68.7324	68.5375	68.5375
B_9^*	85.8128	88	85.1608	85.9823	85.9923	85.9791	85.7944	85.8127
B_{10}^*	105.7750	108	103.514	105.002	105.187	105.084	105.115	105.775
B_{11}^*		130	123.533	125.853	126.282	126.049	126.5	126.82
B_{12}^*		154	145.216	148.536	149.278	148.871	149.948	149.819
B_{13}^*		180	168.564	173.051	174.175	173.553	175.46	177.703
B_{14}^*		208	193.577	199.397	200.972	200.093	203.036	203.738
B_{15}^*		238	220.254	227.576	229.671	228.492	232.676	229.178
B_{16}^*		270	248.597	257.587	260.271	258.750	264.379	268.879

Repeat this process till the minimum possible errors are attained. The obtained polynomials of the best approximation are listed in the following.

For the set $H_n(y)$ $(n \leq 3)$, the polynomial of the best approximation is the CS polynomial

$$\mathcal{H}_3(y) = 1 + y + y^2 - y^3 \tag{16}$$

The CS equation is accurate. It gives the exact second and third virial coefficients. The predicted virial coefficients from B_4 to B_{10} are accurate, with errors of 1.99%, 0.80%, 0.46%, 1.23%, 2.13%, 2.55%, and 2.10%, respectively, as shown in Table I.

For the set $H_n(y)$ $(n \leq 4)$, the polynomial of the best approximation is

$$\mathcal{H}_4(y) = 1 + y + y^2 - 0.6352y^3 - 0.7y^4 \tag{17}$$

The resulting equation of state is accurate. It gives the exact second, third, and fourth virial coefficients. The predicted virial coefficients from B_5 up to B_{10} are accurate, with errors of 0.60%, 0.69%, 0.19%, 0.096%, 0.76%, and 2.14%, respectively, as shown in Table I.

For the set $H_n(y)$ $(n{\leq}5)$, the polynomial of the best approximation is

$$\mathcal{H}_5(y) = 1 + y + y^2 - 0.6352y^3 - 0.8699y^4 + 0.337y^5 \tag{18}$$

The resulting equation of state is very accurate. It gives the exact virial coefficients up to the fifth. The predicted virial coefficients from B_6 up to B_{10} are very accurate, with errors of 0.25%, 0.18%, 0.38%, 0.20%, and 0.73%, respectively, as shown in Table I.

For the set $H_n(y)$ $(n{\leq}6)$, the polynomial of the best approximation is

$$\mathcal{H}_6(y) = 1 + y + y^2 - 0.6352y^3 - 0.8699y^4 + 0.236y^5 + 0.17y^6 \tag{19}$$

The resulting equation of state is very accurate. It gives the exact virial coefficients up to the sixth. The predicted virial coefficients from B_7 up to B_{10} are very accurate, with errors of 0.07%, 0.23%, 0.21%, and 0.56%, respectively, as shown in Table I.

For the set $H_n(y)$ $(n{\leq}7)$, the polynomial of the best approximation is

$$\mathcal{H}_7(y) = 1 + y + y^2 - 0.6352y^3 - 0.8699y^4 + 0.236y^5 + 0.2078y^6 - 0.08y^7 \tag{20}$$

The resulting equation of state is very accurate. It gives the exact virial coefficients up to the seventh. The predicted virial coefficients B_8, B_9, and B_{10} are very accurate, with errors of 0.28%, 0.19% and 0.65%, respectively, as shown in Table I.

For the set $H_n(y)$ $(n{\leq}8)$, the polynomial of the best approximation is

$$\mathcal{H}_8(y) = 1 + y + y^2 - 0.6352y^3 - 0.8699y^4 + 0.236y^5 + 0.2078y^6 - 0.2749y^7 + 0.4y^8 \tag{21}$$

The resulting equation of state is very accurate. It gives the exact virial coefficients up to the eighth. The predicted virial coefficients B_9 and B_{10} are very accurate, with errors of 0.021% and 0.62%, respectively, as shown in Table I.

The known virial coefficients [21] and the predictions made by use of $\mathcal{H}_3, \cdots, \mathcal{H}_8$ and the Padé approximation [5/4] are listed in Table I. For the unknown virial coefficients from B_{11}^* up to B_{16}^*, these predictions are close to each other.

III. COMPARISON

The simulation values of $P/\rho k_{\rm B}T$ for $0.100{\leq}\rho a^3{\leq}0.995$ on the stable fluid branch obtained by Banner-

DOI:10.1088/1674-0068/23/06/675-679

TABLE II Values of $P/\rho k_{\rm B}T$ on the stable($0\leq\rho a^3\leq0.940$) and metastable($0.950\leq\rho a^3\leq0.990$) fluid branch for a hard-sphere fluid.

ρa^3	Simu.	$\mathcal{H}_3$	$\mathcal{H}_4$	$\mathcal{H}_5$	$\mathcal{H}_6$	$\mathcal{H}_7$	$\mathcal{H}_8$	[5/4]
0.100	1.2397243(69)	1.23967	1.23972	1.23972	1.23972	1.23972	1.23972	1.23972
0.200	1.5536109(77)	1.55317	1.55363	1.55361	1.55361	1.55361	1.55361	1.55361
0.300	1.968242(26)	1.96671	1.96836	1.96824	1.96823	1.96823	1.96823	1.96823
0.400	2.521648(39)	2.518	2.52206	2.52167	2.52162	2.52162	2.52162	2.52162
0.500	3.269361(52)	3.26243	3.27053	3.26957	3.2694	3.26942	3.2694	3.2694
0.600	4.294940(10)	4.28342	4.29735	4.29541	4.29496	4.295	4.29493	4.29496
0.700	5.726860(15)	5.71021	5.73117	5.72788	5.72687	5.72695	5.72679	5.7269
0.750	6.655210(25)	6.63606	6.66037	6.65638	6.65495	6.65505	6.65481	6.65502
0.800	7.769970(27)	7.74969	7.7765	7.77199	7.77004	7.77015	7.76984	7.77022
0.850	9.118670(26)	9.0988	9.12628	9.12171	9.11912	9.11922	9.11887	9.11953
0.900	10.76295(36)	10.7461	10.7709	10.7672	10.7639	10.7639	10.7637	10.7648
0.910	11.13401(21)	11.1183	11.1419	11.1385	11.1351	11.1351	11.1349	11.1361
0.920	11.52173(17)	11.5064	11.5286	11.5257	11.5221	11.522	11.5219	11.5233
0.930	11.92585(24)	11.9114	11.9318	11.9294	11.9257	11.9256	11.9256	11.927
0.940	12.34879(59)	12.334	12.3525	12.3506	12.3468	12.3467	12.3468	12.3483
0.950	12.79133(40)	12.7753	12.7914	12.7903	12.7864	12.7861	12.7864	12.7881
0.960	13.25395(94)	13.2362	13.2496	13.2493	13.2453	13.245	13.2454	13.2473
0.970	13.73966(88)	13.7179	13.7281	13.7288	13.7247	13.7243	13.7249	13.7269
0.975	13.9912(16)	13.9669	13.9754	13.9766	13.9724	13.9719	13.9727	13.9748
0.980	14.24832(74)	14.2215	14.2281	14.2299	14.2257	14.2251	14.226	14.2282
0.990	14.7843(12)	14.7482	14.7506	14.7537	14.7494	14.7488	14.7499	14.7523
0.995	15.06266(92)	15.0206	15.0207	15.0245	15.0202	15.0195	15.0208	15.0232

man *et al.* [14] are listed in Table II. The theoretical values predicted by use of $\mathcal{H}_3$, $\cdots$, $\mathcal{H}_8$ and the Padé approximation [5/4] are also listed in Table II. We see that the CS equation of state given by $\mathcal{H}_3$ slightly underestimates the pressures, with maximum error 0.29% occurring at $0.700\leq\rho a^3\leq0.750$. The equation of state given by $\mathcal{H}_4$ slightly overestimates the pressures, with maximum error 0.084% occurring at $0.800\leq\rho a^3\leq0.850$. The maximum error of the equation of state given by $\mathcal{H}_5$ is 0.040% occurring at $0.900\leq\rho a^3\leq0.910$. The maximum error of the equation of state given by $\mathcal{H}_6$ is 0.016% occurring at ρa^3=0.940. The maximum error of the equation of state given by $\mathcal{H}_7$ is 0.017% occurring at ρa^3=0.940. The maximum error of the equation of state given by $\mathcal{H}_8$ is 0.016% occurring at ρa^3=0.940. The higher the order of the polynomial of the best approximation is, the more accurate the resulting equation of state is.

Since these equations of state are obtained by use of the known virial coefficients, we do not expect that they should be accurate on the metastable fluid branch. To our surprise, they are indeed accurate on the metastable fluid branch for $0.950\leq\rho a^3\leq0.995$. Their errors increase with increasing density, with maximum errors about 0.26 % occurring at ρa^3=0.995. They only slightly underestimates the pressures. Of these equations of state, the most accurate are those given by $\mathcal{H}_4$ and $\mathcal{H}_5$. We should point out that these equations of state will fail entirely at the density of the random close-packing state. The reason is as follows. The metastable fluid branch starts at the freezing point and ends at the random close-packing state $y=y_{\rm rcp}=0.644\pm0.005$ [28]. As the random close-packing state (rcp) is approached, the pressure diverges as $(y_{\rm rcp}-y)^{-1}$. However, these equations of state predict that the pressure does not diverge at $y=y_{\rm rcp}$ and diverges at the unphysical state y=1. Therefore these equations of state will fail entirely at the density of the random close-packing state.

IV. CONCLUSION

Very accurate numerical results for hard-sphere systems have been obtained in recent years. Labik *et al.* have obtained the virial coefficients up to B_9. Clisby and McCoy have obtained the virial coefficients up to B_{10}. Bannerman *et al.* have obtained the pressures on the stable fluid branch and on the metastable fluid branch.

These very accurate numerical results reveal that the CS equation is not very accurate. The CS equation needs to be improved. For hard-sphere fluids, the pressure is a continuous function of density in the whole fluid regime. Weierstrass's theorem, Chebyshev's theorem, and referring to the equations of state of the scaled-particle theory and the Percus-Yevick integration equa-

DOI:10.1088/1674-0068/23/06/675-679

tion, demonstrate that there exists a sequence of polynomials such that the equation of state is given by the limit of the sequence of polynomials. The polynomials of the best approximation from the third order up to the eighth order are obtained. The third-order polynomial of the best approximation is precisely the CS polynomial. So the CS equation is not a lone result and can be improved successively. The resulting equations of state are in good agreement with the simulation results on the stable fluid branch. The higher the order of the polynomial of the best approximation is, the more accurate on the stable fluid branch the resulting equation of state is. Although these equations of state are obtained by use of the known virial coefficients, we are surprised at finding that they are still accurate for $\rho a^3 \leq 0.995$ on the metastable fluid branch.

V. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No.10874111).

[1] (a) X. Z. Wang, J. Chem. Phys. **123**, 054504 (2005).
(b) X. Z. Wang, Phys. Rev. E **66**, 056102 (2002).
(c) X. Z. Wang, Physica A **380**, 163 (2007).
[2] L. Tonks, Phys. Rev. **50**, 955 (1936).
[3] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960).
[4] B. J. Alder and T. E. Wainwright, Phys. Rev. **127**, 359 (1962).
[5] B. J. Alder, W. G. Hoover, and D. A. Young, J. Chem. Phys. **49**, 3688 (1968).
[6] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).
[7] (a) X. Z. Wang, Phys. Rev. E **66**, 031203 (2002);
(b) X. Z. Wang, J. Chem. Phys. **120**, 7055 (2004).
[8] X. Z. Wang, J. Chem. Phys. **122**, 044515 (2005).
[9] A. S. Kraemer and G. G. Naumis, J. Chem. Phys. **128**, 134516 (2008).
[10] L. L. Lee, *Molecular Thermodynamics of Nonideal Fluids*, Chap. VIII, Boston: Buterworths, (1988).
[11] A. Mulero, M. I. P. C. A. Galán, and F. Cuadros, *Theory and Simulations of Hard-Sphere Fluids and Related Systems*, Lecture Notes in Physics Vol.753, Berlin: Springer-Verlag, (2008).
[12] (a) X. Z. Wang, Physica A **341**, 433 (2004).
(b) X. Z. Wang, Eur. Phys. J. B **48**, 385 (2005).
(c) X. Z. Wang, J. Phys. A **42**, 265001 (2009).
[13] G. Bryant, S. R. Williams, L. Qian, I. K. Snook, E. Perez, and F. Pincet, Phys. Rev. E **66**, 060501 (2002).
[14] M. N. Bannerman, L. Lue, and L. V. Woodcock, J. Chem. Phys. **132**, 084507 (2010).
[15] (a) J. W. Hu and Y. X. Yu, Chin. Phys. Lett. **26**, 086404 (2009).
(b) J. W. Hu and Y. X. Yu, Phys. Chem. Chem. Phys. **11**, 9382 (2009).
[16] X. Z. Wang, Physica A **389**, 3048 (2010).
[17] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).
[18] F. H. Ree and W. Hoover, J. Chem. Phys. **40**, 939 (1964).
[19] J. A. Barker and D. Henderson, Mol. Phys. **21**, 187 (1971).
[20] S. Labik, J. Kolafa, and A. Malijevský, Phys. Rev. E **71**, 021105 (2005).
[21] N. Clisby and B. M. McCoy, J. Stat. Phys. **122**, 15 (2006).
[22] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).
[23] E. Helfand, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **34**, 1037 (1961).
[24] M. S. Wertheim, J. Math. Phys. **5**, 643 (1964).
[25] E. Thiele, J. Chem. Phys. **39**, 474 (1964).
[26] X. Z. Wang, J. Phys.: Condens. Matter **20**, 295207 (2008).
[27] G. G. Lorentz, *Approximation of Functions*, New York: Holt, Rinehart, and Winston, (1966).
[28] M. D. Rintoul and S. Torquato, Phys. Rev. Lett. **77**, 4198 (1996).

DOI:10.1088/1674-0068/23/06/675-679