A general equation of state for hard hyperspheres

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Based on an observation of the Carnahan-Starling equation of state for hard sphere fluid and its generalization to arbitrary dimensions, a new simple equation of state for hard hyperspheres is proposed. Accuracy of the new equation is then tested in dimensions ≤ 8 by comparison with results from computer simulation data. In all dimensions, the proposed equation demonstrated comparable accuracy with previously established equations.

I. INTRODUCTION

There has been increased interest in hard hyperspheres in recent years [1-9]. The simple functional form of their potential functions allows for the possibility, with respect to other potentials, of calculating their virial coefficients by analytical and numerical methods, [10-13] the results of which are then able to be compared with those from computer simulations. The equation of state is obtainable from virial coefficients using, for example, the Padé approximation method. Many equations of state for hard hyperspheres have been devised using this approach; each valid, however, only for the particular relevant dimension.

In this paper, based on generalization of an observation of the famous Carnahan-Starling equation [14], we obtain a general equation of state for hard hyperspheres derived from knowing only up to the fourth virial coefficients, uniform and valid at any dimension. The behavior of hard spheres in higher dimensions has been studied extensively over the years with varying degrees of success; for example, Clisby *et al.* have calculated higher virial coefficients of a hard hypersphere both analytically and numerically [11-13]. Bishop and Whitlock [15] performed Monte Carlo simulations for hard hyperspheres up to $d \le 8$, where d represents the dimensionality of the system, also obtaining various equations of state for hard hyperspheres by the Padé approximation method, using up to seven previously calculated virial coefficients, and comparing these with their Monte Carlo results. Following on from these elaborate investigations, we propose to develop a simple general form equation of state for hard hyperspheres in all dimensions using an approach, as illustrated previously [16], using only second, third, and fourth virial coefficients. These virial coefficients may be calculated analytically in almost all dimensions [10]. In a subsequent section, we proceed to rewrite the well-known Carnahan-Starling equation for hard sphere in dimension three in a form which may be demonstrated to be a cubic polynomial of a new variable. The method is conceived to be useful at any dimension, hence the generalized equation are then derived, in the ensuing section, and compared with existing computer simulation data.

II. THE METHOD

The Carnahan-Starling equation for hard sphere fluid is

$$Z = \frac{\eta^3 - \eta^2 - \eta - 1}{(\eta - 1)^3} \tag{1}$$

where Z and η are the compressibility factor and the packing fraction of the fluid, respectively. Eq. (1) can be rewritten in the following form:

$$Z = 1 - 2\zeta - 2\zeta^3 \tag{2a}$$

where

$$\zeta = \frac{1}{1-\eta} \tag{2b}$$

which clearly shows that the Carnahan-Starling equation may be considered as a cubic polynomial of a new variable ζ. Similar observation may be made for the accurate Henderson equation for hard disks [17]. Because of the success of the method (i.e., expressing the compressibility factor as a cubic polynomial of ζ) to find accurate equation of state for hard disks and spheres, one may be tempted to use the method in any dimension. We therefore suppose that the compressibility factor of hard hypersphere fluid is a cubic polynomial with respect to ζ :

$$Z = a_0 + a_1\zeta + a_2\zeta^2 + a_3\zeta^3 \tag{3}$$

in which a's are unknowns to be determined and $\zeta = \frac{1}{1-\eta}$.

Four parameters a_0, a_1, a_2, a_3 may be determined simply by expanding Eq. (3), and comparing these with the virial series in ascending power of η:

$$Z = 1 + b_2\eta + b_3\eta^2 + b_4\eta^3 + \ldots \tag{4}$$

to find a system of solvable equations. After inserting the calculated values in Eq. (3), and expressing them in closed form, we finally obtain a unique equation of state for hard hyperspheres:

$$Z = \frac{(1-3b_2+3b_3-b_4)\eta^3 + (-3+3b_2-b_3)\eta^2 + (3-b_2)\eta - 1}{(\eta-1)^3}. \tag{5}$$

This is the desired cubic equation for hard hyperspheres that uses only the first four virial coefficients of hard hyperspheres. As soon as the first four virial coefficients in any dimension are known, Eq. (5) may be used to obtain an equation for hard hyperspheres in that dimension. At dimension three, this is precisely Eq. (1), provided one uses $b_4 = 18$ instead of 18.36 as Carnahan and Starling did. If one uses the exact value of b_4, the following equation has been obtained:

$$Z = \frac{0.64\eta^3 - \eta^2 - \eta - 1}{(\eta-1)^3}. \tag{6}$$

Accuracy of Eqs. (1) and (6), as well as a number of others, has been considered [16]. Eq. (5) may be conceived as a generalized Carnahan-Starling equation for hard hyperspheres. In dimension two it reduces to Henderson equation for hard disks [18]. Since Carnahan-Starling and Henderson equations represent accurately the behaviors of hard spheres and hard disks fluid, it is expected that their generalization, Eq. (5), would be able to represent the behavior of hard hyperspheres as well. It will be seen that even though Eq. (5) (in a given dimension) is not the most accurate of the equations especially designed for hard hyperspheres at any dimension, it is as accurate as a large number of them while it is, at the same time, very simple and promising. In the next section, we will find the equation for hard hyperspheres at dimensions four to eight so that their required virial coefficients and computer simulation data are known exactly in order to examine the accuracy of the proposed equation, Eq. (5).

III. RELIABILITY OF THE EQUATION OF STATE FOR HARD HYPERSPHERES AT DIMENSIONS ≥ 4

In order to find the reliability of Eq. (5) in each dimension, one needs to know the first four virial coefficients. Many attempts have been made to calculate virial coefficients of hard hyperspheres both analytically and numerically [10-13]. Table I shows the required values. Using these values together with the general relation between the packing fraction and the reduced number density in dimension d, i.e., $\eta = \dfrac{\pi^d \rho}{2^d \Gamma\left(1+\dfrac{d}{2}\right)}$ one finds the desired equation at any dimension:

$$Z = \frac{-1 - 3.5278\eta^3 - 11.4058\eta^2 - 5\eta}{(\eta-1)^3} \tag{7a}$$

and

$$Z = \frac{-1 - 0.0001076599121\pi^6\rho^3 - 0.01113847656\pi^4\rho^2 - \frac{5}{32}\pi^2\rho}{\left(\frac{\pi^2\rho}{32} - 1\right)^3} \tag{7b}$$

for hard 4-spheres;

$$Z = \frac{-1 - 40.1833\eta^3 - 61\eta^2 - 13\eta}{(\eta-1)^3} \tag{8a}$$

and

$$Z = \frac{-1 - 0.0001860337963\pi^6\rho^3 - \frac{61}{3600}\pi^4\rho^2 - \frac{13}{60}\pi^2\rho}{\left(\frac{\pi^2\rho}{60} - 1\right)^3} \tag{8b}$$

for hard 5-spheres;

$$Z = \frac{-1 - 140.8756\eta^3 - 256.1226\eta^2 - 29\eta}{(\eta-1)^3} \tag{9a}$$

and

$$Z = \frac{-1 - 0.248795262110^{-5}\pi^9\rho^3 - 0.001736942546\pi^6\rho^2 - \frac{29}{384}\pi^2\rho}{\left(\frac{\pi^3\rho}{384} - 1\right)^3} \tag{9b}$$

for hard 6-spheres;

$$Z = \frac{-1 + 690.9634\eta^3 - 967\eta^2 - 61\eta}{(\eta - 1)^3} \tag{10a}$$

and

$$Z = \frac{-1 + 0.116578157110^{-5}\pi^9\rho^3 - \frac{967}{705600}\pi^6\rho^2 - \frac{61}{840}\pi^2\rho}{\left(\frac{\pi^3\rho}{840} - 1\right)^3} \tag{10b}$$

for hard 7-spheres;
and finally in dimension eight:

$$Z = \frac{-1 + 16512.3943\eta^3 - 3462.8502\eta^2 - 125\eta}{(\eta - 1)^3} \tag{11a}$$

and

$$Z = \frac{-1 + 0.711961369010^{-7}\pi^{12}\rho^3 - 0.00009173420270\pi^8\rho^2 - \frac{125}{6144}\pi^4\rho}{\left(\frac{\pi^4\rho}{6144} - 1\right)^3}. \tag{11b}$$

TABLE I. Virial coefficients at various dimensions obtained from [3].

Dimension	4	5	6	7	8
b2	8	16	32	64	128
b3	32.4058	106	349.1226	1156	3843.8502
b4	77.7452	311.1833	1093.2434	2586.0366	-5363.8437

Tables II, III, IV, V and VI show the comparison of Eq. (5) for hard 4-, 5-, 6-, 7-, and 8-spheres, respectively, against the computer simulation data and some relevant proposed equations of state at each dimension. In the tables, we have used the average fractional deviation from the computer simulation data (Z_{CS}) defined as:

$$\Delta = \frac{100\left(\sum_{j=1}^{N}\frac{|Z_{CS}(\eta_j) - Z(\eta_j)|}{Z_{CS}(\eta_j)}\right)}{N}$$

as a measure to find the accuracy of the equations as well as for comparison. As is known from definition, the lesser Δ indicates the better data. Two other general equations which have been used for better comparisons are the Baus-Colot proposal [19]:

$$Z = \frac{1 + (b_2 - d)\eta + \left(b_3 - b_2 d + \frac{d(d-1)}{2}\right)\eta^2}{(1-\eta)^d} \tag{12}$$

and the Song-Mason-Stratt equation [20]:

$$Z = 1 + \frac{b_2\eta\left(1+\left(\frac{b_3}{b_2}-d\right)\eta\right)}{(1-\eta)^d}. \quad (13)$$

As an accurate semiempirical equation of state, one should mention the Luban-Michels [21]:

$$Z = 1 + \frac{b_2\eta\{1+[b_3/b_2-\zeta(\eta)b_4/b_3]\eta\}}{1-\zeta(\eta)(b_4/b_3)\eta+[\zeta(\eta)-1](b_4/b_2)\eta}. \quad (14)$$

Luban and Michels approximated $\zeta(\eta) = a_0 + a_1\eta$. The coefficients can be determined by a least square fitting of computer simulation data. When there were other equations (for example in dimensions 5 and 7) these were also used for comparisons.

These tables reveal that the proposed equation Eq. (5) is more accurate than Eqs. (12) and (13) in all dimensions. Moreover, it also has accuracy and simplicity compared to other proposals especially designed at a given dimension using available computer simulation data, i.e., the latter are, in a way, semi-empirical since they include computer simulation data in their equations. It seems Eq. (5) is as accurate as the Luban-Michels equation, a semi-empirical equation at least at low to moderate densities. The range of computer simulation data reported for dimensions 6, 7, and 8 is "for low to moderate densities" [15] which is also true for dimensions 4 and 5.

In summary, the results in the tables below suggest that although Eq. (5) is not the optimal to represent computer simulation data, it is able to accurately represent hard hyperspheres in a unifying way. It must be noted that only the first four virial coefficients have been invoked at any dimension and the resulting equation is unique. Eq. (5) has the simultaneous merits of simplicity, uniformity, and accuracy.

TABLE II. Comparison of the compressibility factors of the obtained hard 4-spheres equation of state, Eq. (7) with computer simulation (ZSIM) data in [22], Baus-Colot (ZBC), Luban-Michels (Zlm) [22], and Song-Mason, Startt (ZSMS) equations.

ρ	ZSIM	Eq. (7)	ZSMS	ZBC	ZLM
0.2	1.6377	1.6373	1.6386	1.6398	1.63743
0.25	1.8523	1.851	1.8536	1.8561	1.85117
0.3	2.0922	2.0916	2.0966	2.1012	2.0921
0.35	2.3643	2.3626	2.3713	2.379	2.3636
0.4	2.6701	2.6676	2.6817	2.694	2.6694
0.45	3.0147	3.0108	3.0327	3.0514	3.0138
0.5	3.4015	3.3969	3.4297	3.4572	3.402
0.55	3.8404	3.8313	3.879	3.9183	3.8394
0.6	4.3319	4.3202	4.3879	4.4427	4.3326
0.65	4.8821	4.8704	4.9648	5.0397	4.889
0.7	5.5197	5.49	5.6193	5.72	5.5171
0.75	6.2309	6.1881	6.3627	6.4963	6.227
0.8	7.0399	6.9749	7.208	7.3831	7.03
0.85	7.9364	7.8626	8.1705	8.3977	7.9394
0.9	8.9714	8.8648	9.268	9.5603	8.9706
0.95	10.135	9.9974	10.521	10.895	10.1416
1	11.477	11.279	11.955	12.429	11.474
Δ	0	0.5091	1.5897	3.1695	0.0446

TABLE III. Comparison of the compressibility factors of the obtained hard 5-spheres equation of state, Eq. (8) with computer simulation (ZSIM) data in [22], Maeso *et al.* (ZMSAV) [23], Luban-Michels [21], Amoros *et al.* (ZASV) [24], Santos [9], Baus-Colot (ZBC), Song-Mason, Startt (ZSMS) equations.

ρ	ZSIM	Eq. (8)	ZMSAV	ZLM	ZASV	ZS	ZBC	ZSMS
0.2	1.653	1.653	1.653	1.653	1.653	1.653	1.656	1.656
0.4	2.624	2.614	2.617	2.618	2.618	2.616	2.642	2.638
0.6	4.008	3.983	4.003	4.009	4.007	4.000	4.096	4.081
0.8	5.997	5.892	5.964	5.986	5.979	5.964	6.218	6.175
1	8.748	8.518	8.720	8.770	8.758	8.731	9.293	9.192
1.1	10.523	10.169	10.488	10.553	10.548	10.510	11.310	11.163
1.15	11.589	11.094	11.490	11.560	11.561	11.520	12.466	12.291
1.18	12.217	11.684	12.133	12.204	12.219	12.168	13.213	13.018
Δ	0	2.177	0.392	0.166	0.146	0.2961	4.520	3.653

TABLE IV. Comparison of the compressibility factors of the obtained hard 6-spheres equation of state, Eq. (9) with computer simulation (ZSIM) data in [15], Luban-Michels [21], Baus-Colot (ZBC), and Song-Mason, Startt (ZSMS) equations.

ρ	ZSIM	Eq. (9)	ZLM	ZBC	ZSMS
0.1	1.282	1.282	1.282	1.282	1.282
0.2	1.613	1.613	1.613	1.615	1.615
0.3	1.996	1.996	1.999	2.005	2.005
0.4	2.442	2.437	2.443	2.459	2.458
0.5	2.948	2.939	2.946	2.984	2.982
0.6	3.527	3.508	3.533	3.588	3.585
0.7	4.182	4.147	4.200	4.281	4.276
0.8	4.921	4.863	4.911	5.072	5.065
0.9	5.756	5.661	5.739	5.974	5.962
Δ	0	0.527	0.159	1.503	1.423

TABLE V. Comparison of the compressibility factors of the obtained hard 7-spheres equation of state, Eq. (10) with computer simulation (ZSIM) data in [15], Percus-Yevick (compressibility route) (ZPYc), Percus-Yevick (virial route) (ZPYv), Robles *et al.* (ZRHS) [5] and Luban-Michels [21], Baus-Colot (ZBC), and Song-Mason, Startt (ZSMS) equations.

ρ	ZSIM	Eq. (10)	ZPYv	ZPYc	ZRHS	ZLM	ZBC	ZSMS
0.1	1.252	1.252	1.252	1.252	1.252	1.252	1.252	1.252
0.2	1.538	1.537	1.535	1.538	1.538	1.537	1.538	1.538
0.3	1.856	1.854	1.850	1.859	1.858	1.858	1.860	1.860
0.4	2.210	2.206	2.197	2.218	2.215	2.215	2.220	2.220
0.5	2.598	2.592	2.577	2.618	2.611	2.615	2.621	2.621
0.6	3.028	3.014	2.990	3.061	3.050	3.060	3.065	3.064
0.7	3.497	3.472	3.439	3.552	3.532	3.553	3.555	3.554
0.8	4.013	3.968	3.924	4.090	4.062	4.101	4.094	4.093
0.9	4.572	4.502	4.444	4.683	4.642	4.706	4.685	4.683
Δ	0	0.497	1.088	0.930	0.592	0.979	1.000	0.985

TABLE VI. Comparison of the compressibility factors of the obtained hard 8-spheres equation of state, Eq. (11) with computer simulation (ZSIM) data in [15], Luban-Michels [21], Baus-Colot (ZBC), and Song-Mason, Startt (ZSMS) equations.

ρ	ZSIM	Eq. (11)	ZLM	ZBC	ZSMS
0.1	1.213	1.213	1.213	1.213	1.213
0.2	1.447	1.444	1.446	1.445	1.445
0.3	1.697	1.695	1.701	1.699	1.699
0.4	1.968	1.965	1.979	1.973	1.974
0.5	2.257	2.253	2.283	2.270	2.270
0.6	2.568	2.561	2.613	2.590	2.590
0.7	2.901	2.886	2.976	2.933	2.933
0.8	3.257	3.230	3.372	3.301	3.300
0.9	3.630	3.592	3.807	3.694	3.693
Δ	0	0.358	1.641	0.692	0.683

IV. CONCLUSION

With reference to a simple observation of the Carnahan-Starling equation of state for hard sphere fluid and its generalization to arbitrary dimensions, a new simple equation of state for hard hyperspheres has been proposed and its accuracy tested in dimensions ≤ 8, where we have access to computer simulation data for comparison. In all dimensions, the proposed equation demonstrated comparable accuracy with previously established equations.

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