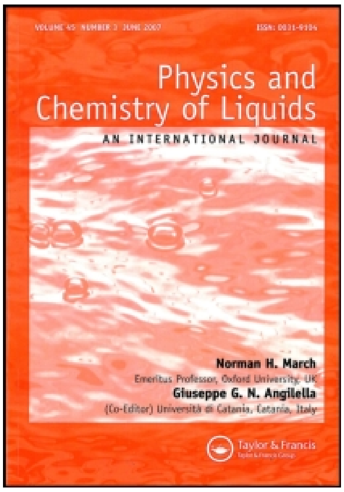

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EQUATIONS OF STATE FOR FOUR- AND FIVE-DIMENSIONAL HARD HYPERSPHERE FLUIDS

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Equations of state for the four- and five-dimensional hard hypersphere fluids have been obtained. Several procedures have been considered in each case: a) adapting the method of Carnahan and Starling to such dimensionalities; b) introducing Padé and Levin approximants suitable to the virial expansion and c) establishing a pole at a given density. In most cases, the results obtained agree satisfactorily with the available simulation data. The use of an additional fitting parameter furnishes nearly perfect agreement.

KEY WORDS: Equations of state, hard hypersphere fluids, packing fraction.

1 INTRODUCTION

The knowledge of the behaviour of hard sphere systems plays an essential role in the context of the properties of matter at high pressures due to the predominance of the repulsive forces over attractive ones. In fact, the hard-sphere potential usually acts as the reference system in the context of perturbative theories used in the study of real fluids. With regard to the equation of state (EOS), this system does not require a complete knowledge of the radial distribution function but only its particular value when the spheres are in contact. Nevertheless, in spite of the evident simplicity of this system, there is no exact solution for the EOS at high or moderate densities (except in one dimension). In the low density range, one may appeal to the virial expansion for the pressure because the first coefficients have been evaluated.

Obviously the dimensionality of the system is not restricted a priori. In fact, calculations of virial coefficients and the evaluation of critical exponents can deal with an arbitrary dimensionality. Notwithstanding, for dimensionalities greater than five, the lack of information concerning the numerical simulation or other type of experimental data prevents the verification of the results.

The objective of the present work is to give simple algebraic EOS which represent the behaviour of the hard hyperspheres system in four and five dimensions for the density range which allows experimental verification to be performed by means of numerical simulation. This range extends to practically the whole stable fluid phase.

This objective is attained by making use of various techniques which have shown their utility in the context of inferior dimensionalities. The results and their implications are given in the next sections.

2 EMPIRICAL EQUATION OF STATE

The use of empirical EOS is of great importance in physical chemistry and chemical engineering. They appear in the domain of real fluids and in their most representative models. Such equations represent an interesting alternative to those deduced from formal theories. Their interest is evident because the Percus-Yevick equation[1] has not been solved analytically for the even values of dimensionality including the hard disk system ($d = 2$).

The virial expansion:

$$Z = \frac{PV}{NkT} = \frac{P}{\rho kT} = 1 + \sum_{i=2} B_i y^{i-1} \tag{1}$$

is nearly always the starting point for determining the EOS. Here, $\rho = N/V$ is the number density of particles and y is the packing fraction, i.e. the ratio between the geometric volume and the volume of the system. In general y may be expressed as:

$$y = N\frac{v_g}{V} = \frac{N}{V}\frac{\pi^{d/2}}{(d/2)!}\left(\frac{\sigma}{2}\right)^d = \frac{\pi^{d/2}}{(d/2)!}\left(\frac{1}{2}\right)^d \rho^* \tag{2}$$

where v_g is the volume of a d-dimensional hard hypersphere, σ its diameter and $\rho^* = N\sigma^d/V$ the reduced density.

Unfortunately, the number of known virial coefficients is limited even for the conventional cases $d = 2, 3$. The situation is more difficult for the higher dimensionalities. For instance, only four coefficients are known for $d = 4$[2-6] and one coefficient more for $d = 5$[2,3,5-7]. With this truncated virial expansion we have calculated Z by means of Eq. (1) and the results appear in Tables 1 and 2, together with the only, to our knowledge, available simulation results[8].

A substantial improvement in three dimensions is due to Carnahan and Starling[9]. In their formulation, the known virial coefficients are approximated by the nearest integer number, obtaining a recurrence formula for reproducting them. Then, they postulate that this relation is fulfilled for every coefficient and they sum the series so obtained. For hard spheres ($d = 3$), the result is:

$$z = \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} \tag{3}$$

Table 1 Equation of state for four-dimensional hard hypersphere fluid.

ρ^*	Z						
	simul.	*virial*	*Eq. (6)*	*Eq. (8)*	*Eq. (11)*	*Eq. (13)*	*Eq. (15)*
0.20	1.637	1.635	1.636	1.636	1.637	1.637	1.637
0.40	2.670	2.626	2.660	2.663	2.668	2.669	2.667
0.60	4.335	4.081	4.300	4.321	4.326	4.331	4.332
0.80	7.038	6.110	6.934	7.019	7.005	7.027	7.011
0.90	8.955	7.374	8.809	8.964	8.923	8.966	8.955
0.95	10.147	8.074	9.932	10.138	10.078	10.136	10.133
1.00	11.458	8.823	11.204	11.473	11.388	11.466	11.478

Table 2 Equation of state for five dimensional hard hypershpere fluid.

ρ^*	Z						
	simul.	*virial*	*Eq. (7)*	*Eq. (9)*	*Eq. (12)*	*Eq. (14)*	*Eq. (15)*
0.20	1.653	1.653	1.653	1.653	1.653	1.653	1.653
0.40	2.624	2.617	2.621	2.619	2.621	2.619	2.618
0.60	4.008	3.997	4.027	4.014	4.031	4.014	4.010
0.80	5.997	5.928	6.061	5.997	6.085	6.000	5.986
1.00	8.748	8.570	9.010	8.782	9.103	8.787	8.766
1.10	10.523	10.215	10.956	10.558	11.123	10.561	10.549
1.15	11.589	11.130	12.077	11.560	12.297	11.558	11.560
1.18	12.217	11.710	12.803	12.199	13.061	12.195	12.207

The validity of this expression is well supported by its excellent agreement with the better numerical simulation data[10].

In spite of the small number of available virial coefficients we have applied this procedure to the case of four and five dimensions, obtaining that those virial coefficients can be approximated by:

$$B_i = 10.5i^2 - 28.5i + 23 \qquad i = 2, 3, 4, \ldots \quad \text{for } d = 4 \tag{4}$$

$$B_i = 59i^3 - 476i^2 + 1349i - 1250 \qquad i = 2, 3, 4, \ldots \quad \text{for } d = 5 \tag{5}$$

Thus, from the sum of the virial series (1),

$$Z = \frac{(1 + 5y + 11y^2 + 4y^3)}{(1 - y)^3} \qquad \text{for } d = 4 \tag{6}$$

$$Z = \frac{(1 + 12y + 48y^2 - 26y^3 + 319y^4)}{(1 - y)^4} \qquad \text{for } d = 5 \tag{7}$$

whose results also appear in Tables 1 and 2.

The agreement is satisfactory, but an improvement is feasible without violating the spirit of the method if one adds a higher order term to the numerators of (6) and (7) because this transformation doesn't modify the known virial coefficients, which are approximated by integers in the procedure. The corresponding coefficient is obtained by means of fitting the simulation data. The expressions obtained are:

$$Z = \frac{(1 + 5y + 11y^2 + 4y^3 + 9.8361y^4)}{(1 - y)^3} \tag{8}$$

$$Z = \frac{(1 + 12y + 48y^2 - 26y^3 + 319y^4 - 923.10y^5)}{(1 - y)^4} \tag{9}$$

The results are shown in Tables 1 and 2. A great improvement in the agreement is found.

The procedure of Carnahan and Starling provides all the virial coefficients but approximates them with integers. This restriction can be removed if one uses the known exact virial coefficients. To do this, an available powerful method is that of Padé approximants[11], which are ratios between two polynomials in the variable y whose coefficients are fixed by stipulating that the expansion of the approximant must reproduce the known virial coefficients.

We have found that none of the possible conventional approximants improve the predictions of the virial expansion, contrary to the two- and three-dimensional cases[12,13]. This is probably due to the small number of known virial coefficients in this case.

We have also tried more sophisticated approximants, such as those of Levin[14,15] and we have verified that the results only improve those of the truncated virial series in the tetradimensional case, although this improvement is not sufficiently satisfactory.

On the other hand, based on the fact that many of the better known EOS for the hard spheres fluid have poles at $y = 1$, it is advantageous to consider Padé approximants which fulfill this condition. This was suggested some years ago by Alder and Hoover[16] and was also shown to be satisfactory for other hard body fluids[17,18].

Moreover, all analytical solutions of the Percus-Yevick equation[19-21] ($d = 1, 3$) and the scaled particle theory (SPT)[22,23] ($d = 1, 2, 3$) have the factor $(1 - y)^d$. Thus, it seems reasonable that the EOS for d-dimensional hard hyperspheres should have the form:

$$Z = \frac{(1 + ay + by^2 + \cdots + ly^\lambda)}{(1 - y)^d} \tag{10}$$

where the coefficients $a, b, \ldots l$ are fixed by identifying the expansion in powers of y with the virial expansion. This expression constitutes a particular case of Padé approximants.

Applying this procedure to our case, we find the following equations for four and five dimensional hard hyperspheres:

$$Z = \frac{(1 + 4y + 6.4032y^2 - 8.1049y^3)}{(1 - y)^4} \tag{11}$$

$$z = \frac{(1 + 11y + 36y^2 - 74.44y^3 + 347.13y^4)}{(1 - y)^5} \tag{12}$$

The results obtained are shown in Tables 1 and 2. Again the accuracy of the results may be increased by adding to the numerator a term in the next power of y whose coefficient is fitted to the simulation data. The following expressions are obtained:

$$Z = \frac{(1 + 4y + 6.4032y^2 - 8.1049y^3 + 1.9739y^4)}{(1 - y)^4} \tag{13}$$

$$Z = \frac{(1 + 11y + 36y^2 - 74.44y^3 + 347.13y^4 - 1068.56y^5)}{(1 - y)^5} \tag{14}$$

whose results also appear in Tables 1 and 2.

3 THE PRESSURE DIVERGENCE

Any EOS that presents only one pole in the compressibility factor at $y = 1$ is in contradiction with the fact that it is impossible (except in one dimension) to pack spheres without the appearence of interstices among them. This fact suggests that the packing limit is that corresponding to the matter perfectly ordered in its crystalline state at the maximum packing density (regular close packing density). The corresponding packing ratio is perfectly defined in all dimensions[24,25]. On the other hand, since the matter is disordered in the fluid state, another maximum packing density, called random close packing density or Bernal density[26] has been proposed in this context for the hard sphere fluid. This density is lower than that corresponding to the crystalline solid. Both choices have been used[15,27] as the possible poles for the compressibility factor of the hard sphere fluid. Nevertheless, the asymptotic behaviour of the virial expansion for the hard sphere fluid[28] seems to favour the first choice.

Accepting the existence of a pole at regular close packing density, we propose the following EOS for hard hypersphere fluids:

$$Z = 1 + d\frac{y/y_0}{(1 - y/y_0)} + C\frac{y^{d-1}}{(1 - y)^{d-1}} + \sum_i \beta_i y^{i-1} \tag{15}$$

where y_0 is the regular close packing ratio, whose value is $\pi^2/16 = 0.61685$ in the tetradimensional case and $2^{3/2}\pi^2/60 = 0.46526$ in the pentadimensional case. Logically, this value decreases as the dimensionality increases.

Equation (15) has only one fitting parameter C since the remaining parameters β_i are fixed by virtue of their identification with those corresponding to the virial expansion. The upper limit of the sum is equal to the order of the highest known virial coefficients. In our case, this value is 4 and 5 for four- and five-dimensional hard hyperspheres respectively.

The proposed equation has a simple pole in the regular packing density and a multiple pole whose order is $d - 1$ for $y = 1$ in order to preserve the excellent features assigned to the empirical equations with the following values for the parameters:

$$C = 36.300;\ \beta_2 = 1.5154;\ \beta_3 = 21.891;\ \beta_4 = 24.121 \text{ for } d = 4$$

$$C = 200.00;\ \beta_2 = 5.2532;\ \beta_3 = 82.886;\ \beta_4 = 255.915;\ \beta_5 = 663.225 \text{ for } d = 5$$

The corresponding results are shown in Tables 1 and 2. We have verified that the attempt to increase the order of the first pole worsens the results appreciably.

4 DISCUSSION

From the analysis of Tables 1 and 2, one can see that the results obtained from the virial expansion are systematically lower than those of the simulation. This suggests that, at least, the first unknown virial coefficient must be positive, in agreement with the two- and three-dimensional cases. Also, the knowledge of an additional virial coefficient significantly improves the agreement when the dimensionality changes from 4 to 5. In this latter case, the agreement is similar to that of the Carnahan-Starling type EOS.

On the other hand, the results given by the Padé approximant with the pole $y = 1$, are rather different from the simulation data for $d = 5$, although they almost coincide with those obtained by Baus and Colot[5] for the Percus-Yevick compressibility equation. Nevertheless, the introduction of a fitting parameter allows us to obtain practical coincidence with the simulation data. The knowledge of a greater number of virial coefficients would probably make this modification unnecessary.

The introduction of a pole at $y = y_0$ also furnishes an excellent agreement with the simulation results. This is also the case for hard spheres (unpublished work) in the domain of the stable fluid phase, and specially in the metastable region[29] where such an equation provides better agreement than an equation with a pole at $y = 1$ exclusively. This situation will probably also be valid in the dimensionalities we are considering, but the lack of simulation data in such regions hinders its verification.

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