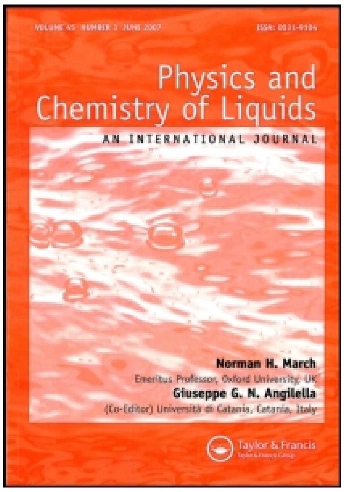


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# Excess Thermodynamic Properties for Hard Sphere Fluids in Several Dimensionalities

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# EXCESS THERMODYNAMIC PROPERTIES FOR HARD SPHERE FLUIDS IN SEVERAL DIMENSIONALITIES

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Equations of state of the algebraic type for the hard disk fluid and the hard sphere fluid have been obtained from recent simulation data. The introduction of a realistic pole furnishes good agreement with the simulation results. The excess thermodynamic properties (entropy, enthalpy and Gibbs free energy) have been calculated, together with those of four and five dimensional hard hypersphere fluids whose equations of state have been proposed in an earlier work. All the results show excellent compatibility with the available information.

KEY WORDS: Excess thermodynamic properties, hard sphere fluids, equations of state.



## 1 INTRODUCTION

In a recent work[1] we have proposed distinct equations of state (EOS) which adequately represent the behaviour of four- and five-dimensional hard hypersphere fluids. Here we complete this study with the treatment of the remaining accesible dimensionalities ($d = 2{,}3$), whose interest is greater owing to their closer approximation to the real world. Although Carnahan and Starling[2] found an EOS which is difficult to improve, the simulation data available at present allow slight modifications to be made in order to increase the agreement.

On the other hand, we have evaluated the excess thermodynamic properties, relative to those of an ideal gas at the same temperature and pressure for all possible dimensionalities.

This allows us to obtain a complete table of the major equilibrium properties for the whole stable range of the hard hypersphere fluid. Although these results are not comparable with direct experimental data, their validity must be equivalent to, or perhaps greater than, the original EOS because the excess entropy depends more on the lower-order virial coefficients than on the higher ones, as compared to the EOS[3].

## 2 THEORETICAL BACKGROUND

The great majority of the EOS proposed for representing the behaviour of the hard sphere fluid may be included in two analytical forms, independently of its dimensionality.

In the first, the compressibility factor $Z = PV/NkT$ is expressed as the ratio between two polynomials, usually in the form:

$$Z = \sum_{i=1}^{m} a_i y^{i-1}/(1-y)^n \tag{1}$$

where $y$ 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, $\sigma$ its diameter and $\rho^* = N\sigma^d/V$ the reduced density.

This expression for $Z$ represents mathematically a particular case of a Padé approximant[4] and includes all the Carnahan-Starling type variants.

The second form is really an improvement of the former, made by introducing the existence of a pole in the compressibility factor for the regular close packing density[5]. This quantity may then be expressed in the form:

$$Z = 1 + d\frac{y/y_0}{1-(y/y_0)} + C\frac{y^{d-1}}{(1-y)^{d-1}} + \sum_i \beta_i y^{i-1} \tag{3}$$

where $y_0$ is the regular close packing ratio. This equation has a unique fitting parameter $C$ because the others are fixed identifying them with those of the virial expansion.

On the other hand, the expressions corresponding to the excess thermodynamic properties depend on the thermodynamic representation employed, that is to say, on the thermodynamic variables utilized. In the representation $T$-$P$, the resulting excess entropy is:

$$\frac{S-S^0}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P \frac{Z-1}{P}\,dP \tag{4}$$

As this is the representation which is experimentally most accessible, it is the one most frequently found in thermodynamics textbooks[6,7].

However, the $T$-$V$ representation is more suitable for our study because the hard sphere EOS appears in this form.

Nevertheless, the difference in the entropy of the two systems is evaluated for the same pressures and temperatures.

The excess entropy is now[8]:

$$\frac{S-S^0}{R} = T\int_\infty^V \left(\frac{\partial Z}{\partial T}\right)_V \frac{dV}{V} + \int_\infty^V \frac{Z-1}{V}\,dV + \ln Z \tag{5}$$

In our case, this expression allows a later simplification to be made since $Z$ does not depend on the temperature for hard-sphere systems.

Therefore, the final result is:

$$\frac{S - S^0}{R} = \ln Z - \int_0^y \frac{Z - 1}{y} dy \tag{6}$$

The determination of the remaining functions of state is straightforward. In fact, since the hard sphere EOS is of the form: $P = Tf(V)$, from thermodynamics, one finds $(\partial U/\partial V)_T = 0$ and $(\partial U/\partial P)_T = 0$, then

$$\frac{U - U^0}{RT} = 0 \tag{7}$$

From this definition:

$$\frac{F - F^0}{RT} = \frac{U - U^0}{RT} - \frac{S - S^0}{R} \tag{8}$$

and for hard spheres:

$$\frac{F - F^0}{RT} = -\frac{S - S^0}{R} \tag{9}$$

The excess enthalpy and the excess Gibbs free energy are equal to:

$$\frac{H - H^0}{RT} = \frac{U - U^0}{RT} + \frac{PV - RT}{RT} = Z - 1 \tag{10}$$

$$\frac{G - G^0}{RT} = \frac{H - H^0}{RT} - \frac{S - S^0}{R} = Z - 1 - \ln Z + \int_0^y \frac{Z - 1}{y} dy \tag{11}$$



## 3 EQUATION OF STATE

In this section our results concerning the EOS for each analyzed system are presented in order of increasing dimensionality.

### *a) Hard Disks*

The first interesting EOS is due to scaled particle theory (SPT)[9]:

$$Z = 1/(1 - y)^2 \tag{12}$$

later modified by Henderson[10]:

$$Z = (1 + 0.125y^2)/(1 - y)^2 \tag{13}$$

and Kratky[11]:

$$Z = (1 + 0.112y^2)/(1 - y)^2 \tag{14}$$

As can be seen, both equations have only one fitting parameter. This parameter is fixed in order to obtain minimum deviation of $Z$ from the best available simulation data, probably those of Erpenbeck and Luban[12]. Thus, one obtains:

$$Z = (1 + 0.083114y^2)/(1 - y)^2 \tag{15}$$

Henderson and Kratky also proposed other equations[13,11] with two parameters:

$$Z = \frac{1 + 0.128y^2}{(1 - y)^2} - \frac{0.043y^4}{(1 - y)^3} \tag{16}$$

$$Z = \frac{1 + 0.12802y^2}{(1 - y)^2} - \frac{0.03003y^3}{(1 - y)^3} \tag{17}$$

Verlet and Levesque[14] have also contributed an equation of the same type:

$$Z = \frac{1 + 0.125y^2}{(1 - y)^2} - \frac{2^{-5}y^4}{(1 - y)^4} \tag{18}$$

Baus and Colot[15] have joined all these equations in the following:

$$Z = \frac{1 + ay^2}{(1 - y)^2} - b\frac{y^{3+c}}{(1 - y)^{2+d}} \tag{19}$$

We have fitted all these equations to the mentioned simulation data and we have found the best agreement with Henderson's expression but with slightly different coefficients:

$$Z = \frac{1 + 0.12651y^2}{(1 - y)^2} - \frac{0.03918y^4}{(1 - y)^3} \tag{20}$$

The comparison with the simulation is shown in Table 1. On the other hand, the available virial coefficients in this case[11,16] set the number of the terms for Eq. (3),

**Table 1** Results of the empirical equations for hard disk fluid.

| $A/A_0$ | 30.0 | 20.0 | 10.0 | 5.0 | 3.0 |
|---|---|---|---|---|---|
| $Z_{sim.}$ | 1.06337 | 1.09743 | 1.21068 | 1.4983 | 2.0771 |
| $Z^*$ | 1.06344 | 1.09753 | 1.21067 | 1.4984 | 2.0771 |
| $Z^{**}$ | 1.06337 | 1.09743 | 1.21068 | 1.4984 | 2.0773 |
| $A/A_0$ | 2.0 | 1.8 | 1.6 | 1.5 | 1.4 |
| $Z_{sim.}$ | 3.4243 | 4.1715 | 5.4964 | 6.6075 | 8.306 |
| $Z^*$ | 3.4246 | 4.1718 | 5.4958 | 6.6074 | 8.3312 |
| $Z^{**}$ | 3.4255 | 4.1727 | 5.4943 | 6.6007 | 8.3111 |

*Eq. (20); **Eq. (21)

which is extended until $i = 7$. Taking into account that $d = 2$ and $y_0 = \pi/2(3)^{1/2} = 0.9069$, the related equation is written as:

$$Z = 1 + 2\frac{y/0.9069}{1-(y/0.9069)} + 4.950\frac{y}{1-y} - 5.155y - 4.254y^2 - 3.374y^3$$
$$-2.570y^4 - 1.845y^5 - 1.198y^6 \tag{21}$$

These results are also shown in Table 1. Here the independent variable utilized was the ratio between the area of the system $A$ and that corresponding to regular close packing, $A_0$. Its relation with the original variable $y$ is elementary:

$$A/A_0 = \pi/2(3)^{1/2}y.$$

The reason for this change is due to the direct transcription of the simulation data and to the use of simple numbers.

*b) Hard Spheres*

The majority of empirical EOS are represented by the expression:

$$Z = (1 + y + y^2 - ay^3)/(1 - y)^3 \tag{22}$$

In fact, taking $a = 3$, $a = 0$, $a = 1$ and $a = 1.5$, one obtains the Percus-Yevick pressure and compressibility equations[17], the Carnahan-Starling (CS) equation[2] and the Mansoori, Provine and Canfield equation[18], respectively.

More recently, Erpenbeck and Wood[19] have obtained excellent simulation data, which allows it to be checked. Fitting these data to that equation furnishes $a = 0.9508$ which is close to the Carnahan-Starling value, confirming once again the superiority of their equation.

An improvement in the results is observed when an additional parameter is introduced. Therefore, we have considered an equation of the form:

$$Z = (1 + y + y^2 - ay^3 - by^4)/(1 - y)^3 \tag{23}$$

and we have fitted the parameters to simulation data cited above, obtaining: $a = 0.64994$; $b = 0.70034$.

The results are shown in Table 2.

**Table 2** Results for the empirical equations for hard sphere fluid.

| $V/V_0$ | 25 | 18 | 10 | 5 | 4 |
|---|---|---|---|---|---|
| $Z_{sim.}$ | 1.12777 | 1.18282 | 1.35939 | 1.88839 | 2.24356 |
| Z* | 1.12775 | 1.18283 | 1.35942 | 1.88849 | 2.24438 |
| Z** | 1.12786 | 1.18284 | 1.35943 | 1.88848 | 2.24431 |
| $V/V_0$ | 3 | 2 | 1.8 | 1.7 | 1.6 |
| $Z_{sim.}$ | 3.03114 | 5.85016 | 7.43040 | 8.60034 | 10.19308 |
| Z* | 3.03190 | 5.85051 | 7.42969 | 8.60014 | 10.19399 |
| Z** | 3.03137 | 5.83892 | 7.37313 | 8.55994 | 10.13040 |

*Eq. (23); **Eq. (24)

The virial coefficients[16,20] are known to the same extent as in the case of hard disks. Therefore, equation (3) is expressed here as:

$$Z = 1 + 3\frac{y/0.7405}{1-(y/0.7405)} + 5.6386(y^2/(1-y)^2) - 0.05142y - 1.1099y^2$$
$$-0.3013y^3 + 1.3302y^4 + 3.8034y^5 + 9.7235y^6 \quad (24)$$

where $d = 3$; $y_0 = (2)^{1/2}\pi/6 = 0.7405$.

The results are also shown in Table 2. They are reported for the variable $V/V_0 = 2^{1/2}\pi/6y$.

Although the first procedure provides better agreement with the simulation data for both hard disks and hard spheres, this trend may not hold in the range of the metastable fluid because the influence of the pole increases. To our knowledge, no simulation has been carried out in this range for hard disks, but Woodcock[21] performed an interesting study on hard spheres for the metastable fluid and even for glass. In this context, we have verified the validity of our statement although the fast increase of the compressibility factor also implies an increase in the dispersion of the simulation.

### c) *Four and Five Dimensional Hard Hyperspheres*

As we pointed out earlier, research on the EOS for these systems was presented in a recent work[1] of the authors.

## 4 EXCESS PROPERTIES

Using the EOS developed in the earlier sections, we have evaluated the excess entropy, excess enthalpy and excess Gibbs free energy by developing the expressions (6), (10) and (11). When the different EOS that have been proposed are analyzed, the results differ among themselves by less than 1%. Therefore, we furnish only one numerical value in each case. Moreover, the absence of direct experimental data does not allow a

**Table 3** Excess quantities for hard disk fluid.

| $A/A_0$ | $\frac{S-S^0}{R} \times 10^4$ | $\frac{H-H^0}{RT} \times 10^3$ | $\frac{G-G^0}{RT} \times 10^3$ |
|---|---|---|---|
| 30.0 | −4.7 | 63.4 | 63.9 |
| 20.0 | −10 | 97.5 | 98.5 |
| 10.0 | −42 | 211 | 215 |
| 5.0 | −200 | 498 | 518 |
| 3.0 | −714 | 1080 | 1150 |
| 2.0 | −2300 | 2420 | 2650 |
| 1.8 | −3250 | 3170 | 3500 |
| 1.6 | −4940 | 4490 | 4990 |
| 1.5 | −6340 | 5600 | 6240 |
| 1.4 | −8450 | 7320 | 8170 |

more rigorous analysis. Our values agree very well with those carried out by Carnahan and Starling[3] using their equation for hard spheres, and with those made by these authors with some other available equations.

On the other hand, all the results show two features that stand out: 1) the absolute value of the differences tends to zero when the volume increases; 2) such differences are always negative for the entropy, which is intuitively evident.

The corresponding results are shown in Tables 3, 4, 5 and 6.

**Table 4** Excess quantities for hard sphere fluid.

| $V/V_0$ | $\frac{S-S^0}{R} \times 10^3$ | $\frac{H-H^0}{RT} \times 10^2$ | $\frac{G-G^0}{RT} \times 10^2$ |
|---|---|---|---|
| 25 | −2.8 | 12.8 | 13.1 |
| 18 | −5.5 | 18.3 | 18.8 |
| 10 | −19.3 | 35.9 | 37.9 |
| 5 | −90.2 | 88.8 | 97.9 |
| 4 | −153 | 124 | 140 |
| 3 | −311 | 203 | 234 |
| 2 | −938 | 484 | 578 |
| 1.8 | −1290 | 640 | 769 |
| 1.7 | −1540 | 758 | 912 |
| 1.6 | −1880 | 916 | 1100 |

**Table 5** Excess quantities for four dimensional hard hypersphere fluid.

| $\rho^*$ | $\frac{S-S^0}{R} \times 10^2$ | $\frac{H-H^0}{RT} \times 10$ | $\frac{G-G^0}{RT} \times 10$ |
|---|---|---|---|
| 0.20 | −6.89 | 6.37 | 7.06 |
| 0.40 | −31.1 | 16.7 | 19.8 |
| 0.60 | −79.0 | 33.3 | 41.2 |
| 0.80 | −160 | 60.2 | 76.2 |
| 0.90 | −217 | 79.6 | 101 |
| 0.95 | −251 | 91.3 | 116 |
| 1.00 | −289 | 104.7 | 130 |

**Table 6** Excess quantities for five dimensional hard hypersphere fluid.

| $\rho^*$ | $\frac{S-S^0}{R} \times 10^2$ | $\frac{H-H^0}{RT} \times 10$ | $\frac{G-G^0}{RT} \times 10$ |
|---|---|---|---|
| 0.20 | −8.51 | 6.53 | 7.38 |
| 0.40 | −35.4 | 16.2 | 19.7 |
| 0.60 | −83.0 | 30.1 | 38.4 |
| 0.80 | −155 | 49.9 | 65.4 |
| 1.00 | −256 | 77.8 | 103 |
| 1.10 | −320 | 95.5 | 128 |
| 1.15 | −356 | 106 | 141 |
| 1.18 | −378 | 112 | 150 |

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