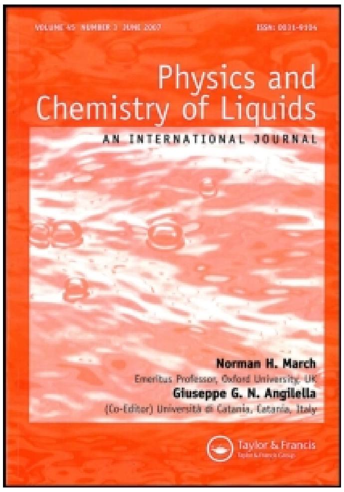

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THERMODYNAMICS OF A FLUID OF HARD D-DIMENSIONAL SPHERES: PERCUS–YEVICK AND CARNAHAN–STARLING-LIKE RESULTS FOR D = 4 AND 5

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The equations of state (EOS) of four and five dimensional hyperspheres have been calculated using Leutheusser's ansatz. In five dimensions these, and the correlation functions, are compared with the results obtained from the analytic solution of the Percus–Yevick (PY) approximation. It is shown that the ansatz reproduces extremely well the PY results. However, in both approximations neither the virial, Z_V, nor the compressibility, Z_C, EOS reproduce well the available molecular dynamics (MD) results. Yet a linear combination of Z_V and Z_C, following the Carnahan–Starling EOS for hard spheres, are in excellent agreement with the MD results in four and five dimensions.

KEY WORDS: Percus–Yevick theory, D-dimensional systems.

1 INTRODUCTION

D-dimensional systems, besides their intrinsic interest, are the testing grounds for statistical mechanics theories. In the theory of liquids it is widely acknowledged that the quality of the approximate theory worsens with increasing dimensionality. The recent availability of analytic solutions for hard D-spheres in odd dimensions within the Percus–Yevick (PY) approximation[1,2], as well as molecular dynamics (MD) simulations of hard hyperspheres in four and five dimensions[3], has led to a renewed interest in the subject[4–7]. New theoretical developments have taken place in three fronts, namely: a) suitable "interpolation" procedures and/or the development of new constructs to obtain approximate expressions for the correlation functions and thermodynamic properties of hard D-spheres, mostly based on what has been learnt from the PY analytic solutions in odd dimensions (see References 4, 5 and 6); b) the calculation of the equation of state (EOS) of D-hard spheres (References 5, 7); and c) the calculation of pair correlation functions for the same systems (Reference 5).

In this work we are mainly concerned with b), although we shall make a brief reference to a particular aspect of c). In fact we show that a linear combination of the PY virial and compressibility EOS, as proposed by Carnahan and Starling[8] for hard spheres, results in a relatively simple and reliable EOS for hard hyperspheres

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in four and five dimensions. We also present results in $D = 5$ which compare the ansatz for the direct correlation function $c(r)$ proposed by Leutheusser[4] with the PY analytic results.

The layout of the paper is as follows. In Section 2 we present the necessary theory and the results of our calculations. We sum up and discuss our results in Section 3.

2 THEORY AND RESULTS

The virial EOS, $Z_V = (PV/Nk_BT)_V$, for hard D-spheres may be written as

$$Z_V = 1 + 2^{D-1}\eta g(1) \tag{2.1}$$

where $g(1)$ is the value of the pair distribution function at contact, assuming the diameter of the hard D-sphere to be $\sigma = 1$ for convenience. The packing fraction η, defined in terms of the volume of the hard D-sphere of unit radius, $\omega_D = \pi^{D/2}/\Gamma(1 + D/2)$, is given by

$$\eta = \omega_D(\tfrac{1}{2})^D\rho = \frac{\pi^{D/2}}{2^D\Gamma(1 + D/2)}\,\rho \tag{2.2}$$

with ρ denoting the reduced density and Γ the gamma function.

The compressibility EOS, Z_C, is deduced from

$$(k_BT)^{-1}\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{\partial}{\partial \eta}\,[\eta Z_C] \tag{2.3}$$

by integrating over η.

We shall call the "Carnahan–Starling" (CS) EOS[8], Z_{CS}, that obtained by the relation

$$Z_{CS} = \tfrac{2}{3}Z_C + \tfrac{1}{3}Z_V \tag{2.4}$$

Within the PY approximation, $g(1+) = -c(1-)$. Moreover, it has been shown that[9]

$$\frac{dZ_C}{d\eta} = 2^{D-1}g^2(1) \quad \text{and} \quad \frac{d(\eta Z_C)}{d\eta} = -c(0) \tag{2.5}$$

resulting in

$$Z_C = -c(0) - 2^{D-1}\eta c^2(1) \tag{2.6}$$

Whence to obtain Z_V and Z_C for hard D-spheres within the PY approximation reduces to finding the values of the direct correlation function $c(r)$ at contact and at zero separation.

The approach we shall follow below is to use the PY analytic solution for odd dimensional hard D-spheres[1,2], to obtain the EOS for $D = 5$. The results thus obtained will be denoted by a superscript PY. We shall also be using the procedure proposed by Leutheusser[4] to obtain approximate analytic solutions in all dimensions. He has shown that $c(r)$ may be written as*

$$c(r) = c(0) + \rho\omega_{D-1}c^2(1)S(r) \quad \text{for } 0 \leq r < 1 \tag{2.7}$$

with

$$-c(0) = 1 - \rho\omega_D c(1) + \rho^2\omega_{D-1}\omega_D c^2(1)F(1) \tag{2.8}$$

and

$$F(1) = \int_0^1 dr\, r^D S'(r) \tag{2.9}$$

where $S'(r)$ denotes the derivative of $S(r)$. The problem now reduces to finding $S(r)$. Its derivative, $S'(r)$, is an even function of r and—in odd dimensions—is a polynomial in r^2 of order $(D-1)/2$; moreover $S'(r=0) = 1$ in all dimensions. Leutheusser[4] has proposed the following ansatz for $S'(r)$ namely

$$S'(r) = (1 - a^2r^2/4)^{(D-1)/2} \tag{2.10}$$

where a is a function of the packing fraction, $a = a(\eta)$, and it should satisfy the following exact results

$$a(\eta = 0) = 1 \quad \text{and} \quad a(\eta = 1) = 2 \tag{2.11}$$

We follow Leutheusser[4] in obtaining the values of the parameter $a(\eta)$ by using the following expression.

$$S'''(0) = -\frac{D-1}{4} - \frac{2}{D+1}\{[c'(1)]^2 - 2c(1)c''(1) - (D-1)c(1)c'(1)\}/c^2(1) \tag{2.12}$$

along with (2.7) and (2.8). We present below the results of our calculations for EOS, for $D = 4$ and 5, using the above procedure; these will be denoted with a superscript L.

Since Eq. (2.10) gives the exact PY results in $D = 1$ and $D = 3$ but not in other dimensionalities, we compare for $D = 5$ the results of $S(r)$ obtained from the PY analytic solution and from Eq. (2.10).

We now turn to the results.

a) Four-dimensional hyperspheres

Using (2.10) we find

$$S(r) = \frac{3}{4a}\,\text{arc}\sin\left(\frac{ar}{2}\right) - \frac{1}{32a}\left[(4 - a^2r^2)^{1/2}(a^3r^3 - 10ar)\right] \tag{2.13}$$

* Please note that the lhs of Eq. (4) in Reference 4 should be preceeded by a minus sign.

In particular

$$S(1) = \frac{3}{4a} \text{ arc sin}\left(\frac{a}{2}\right) - \frac{1}{32} [(4 - a^2)^{1/2}(a^2 - 10)] \tag{2.14}$$

$$F(1) = \frac{1}{64a^5} \left\{48 \text{ arc sin}\left(\frac{a}{2}\right) - (4 - a^2)^{1/2}(a^7 - 6a^5 + 2a^3 + 12a)\right\} \tag{2.15}$$

and

$$S'''(0) = -\tfrac{3}{4}a^2 \tag{2.16}$$

For each value of η, the corresponding $c(1)$, $C(0)$ and a are obtained inserting these expressions into (2.7), (2.8) and (2.12).

The values of the parameter a as a function of η are shown in Figure 1. With the above results we have evaluated the EOS using both the compressibility, Z_C^L, and virial, Z_V^L, routes respectively; as well as the CS-like EOS, Z_{CS}^L. The results are shown in Table 1 where we have also listed, for comparison, the MD results of Michels and

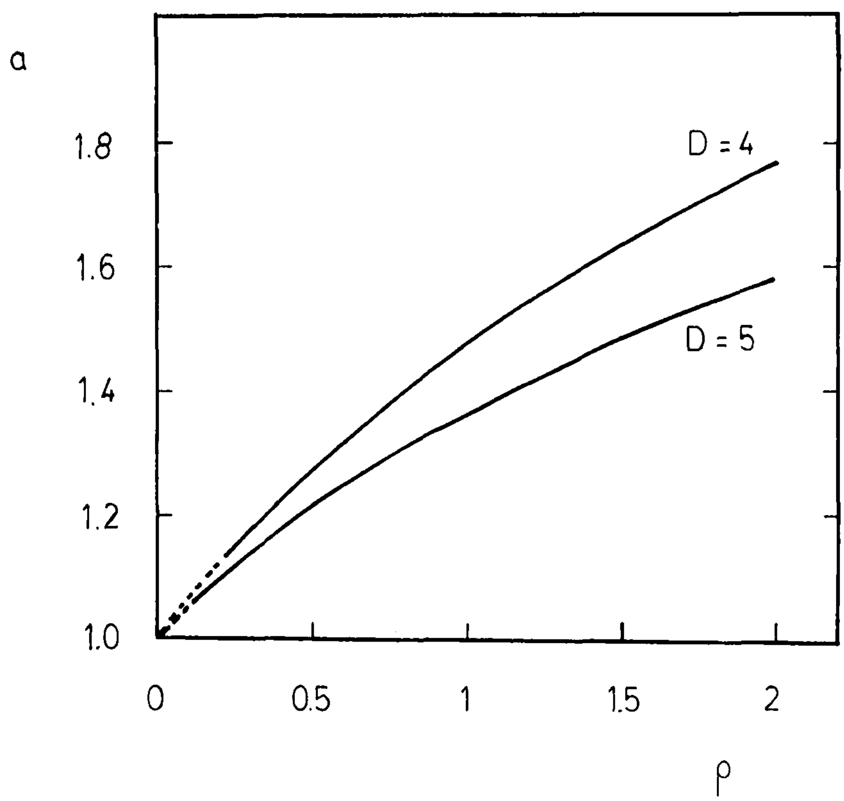

Figure 1 The parameter a in Leutheusser's ansatz for hard hyperspheres, $D = 4$ and 5, as a function of the reduced density ρ.

Table 1 Equation of state for hard hyperspheres, $D = 4$. For the meaning of the symbols heading each column, see text.

ρ	Z_{MT}	Z_V^L	Z_C^L	Z_{CS}^L	Z_{BC}	Z_{ASV}
0.20	1.637	1.6324	1.6392	1.6369	1.6373	1.637
0.40	2.670	2.6214	2.6881	2.6659	2.6682	2.667
0.60	4.335	4.1389	4.4232	4.3284	4.3261	4.332
0.80	7.038	6.4596	7.3454	7.0501	7.0043	7.011
0.90	8.955	8.0503	9.5177	9.0286	8.9229	8.955
0.95	10.147	8.9847	10.8529	10.2302	10.0774	10.133
1.00	11.458	10.0270	12.3914	11.6033	11.3876	11.478

Trappeniers[3], Z_{MT}, the best results obtained by Baus and Colot[5], Z_{BC}, using their ansatz; and the best results obtained by Amorós *et al*[7], Z_{ASV}, using their empirical EOS. We note that Z_C^L and Z_V^L bound the MD results from above and below respectively, but the agreement is not very good and deteriorates with increasing values of η. However the results of Z_{CS}^L are in excellent agreement with the MD results, with an accuracy similar to the parameter free Z_{BC}, although not as accurate as the empirical Z_{ASV} which contains one adjustable parameter.

b) Five-dimensional hyperspheres

At $D = 5$ we are able to compare the PY analytic results with those obtained by using Leutheusser's ansatz, and both with the MD results. From the PY analytic solution we obtain the following EOS

$$Z_V^{PY} = \frac{4(1 + 18\eta + 6\eta^2)^{3/2} + 11 + 87\eta + 393\eta^2 + 9\eta^3}{15(1 - \eta)^3} \tag{2.17}$$

$$Z_C^{PY} = \frac{2(1 + 18\eta + 6\eta^2)^{3/2} - 2 + 135\eta + 1230\eta^2 + 3645\eta^3 + 990\eta^4 + 252\eta^5}{225\eta(1 - \eta)^5} \tag{2.18}$$

and the CS-like EOS obtained from the above reads

$$Z_{CS}^{PY} = \{4(1 + 18\eta + 6\eta^2)^{3/2}(1 + 33\eta - 24\eta^2 + 15\eta^3) - 4 + 3\eta(145 + 1145\eta + 3580\eta^2 - 2709\eta^3 + 2043\eta^4 + 45\eta^5)\}/675\eta(1 - \eta)^5 \tag{2.19}$$

Leutheusser's ansatz leads, for $D = 5$, to the following results

$$S(r) = r\left\{1 - \frac{(ar)^2}{6} + \frac{(ar)^4}{80}\right\} \tag{2.20}$$

$$S(1) = 1 - \frac{a^2}{6} - \frac{a^4}{80} \tag{2.21}$$

$$F(1) = \frac{3a^4 - 30a^2 + 80}{480} \tag{2.22}$$

Table 2 Equation of state for hard hyperspheres, $D = 5$. For the meaning of the symbols heading each column see text.

ρ	Z_{MT}	Z_V^L	Z_V^{PY}	Z_C^L	Z_C^{PY}	Z_{CS}^L	Z_{CS}^{PY}	Z_{BC}	Z_{ASV}
0.20	1.653	1.6486	1.6490	1.6552	1.6554	1.6530	1.6533	1.6527	1.653
0.40	2.624	2.5787	2.5817	2.6354	2.6383	2.6165	2.6194	2.6117	2.618
0.60	4.008	3.8669	3.8713	4.0780	4.0862	4.0076	4.0146	3.9758	4.010
0.80	5.997	5.6194	5.6152	6.1874	6.1973	5.9981	6.0033	5.8746	5.986
1.00	8.748	7.9767	7.9412	9.2669	9.2582	8.8368	8.8192	8.4790	8.766
1.10	10.523	9.4378	9.3733	11.3033	11.2686	10.6814	10.6368	10.1136	10.549
1.15	11.589	10.2506	10.1672	12.4759	12.4218	11.7341	11.6703	11.0248	11.560
1.18	12.217	10.7668	10.6706	13.2349	13.1665	12.4122	12.3345	11.6111	12.207

and

$$S'''(0) = -a^2 \tag{2.23}$$

The values of $a(\eta)$ obtained from Eqs (2.20)–(2.23) are also plotted in Figure 1.

The results for the EOS are shown in Table 2 where we have also included Z_{MT}, Z_{BC} and Z_{ASV} for comparison. Z_V^L and Z_V^{PY} differ by less than 1% whereas Z_C^{PY} and Z_C^L differ, at most, by 0.5%; an indication that Leutheusser's is an extremely good representation of the PY solution. In fact we show in Figure 2 that, on the scale of the Figure, it is almost impossible to set apart the $S(r)$ obtained from the PY solution and the ansatz, to the extent that we indicate the values of the PY solution by crosses superposed on the curve plotting the $S(r)$ given by Eq. (2.20).

As expected when we compare the EOS with the MD results, the virial and compressibility routes give results which are comparatively worse than those obtained for $D = 4$. Once again the two routes bound the MD results. Also the CS-like EOS compares extremely well with the MD results, with that obtained from the PY analytic solution, Z_{CS}^{PY}, marginally better than Z_{CS}^L. Actually the largest difference of either of these two EOS and the results obtained from the MD simulations is about 1.6%, which is smaller than the error bar of the latter Z_{CS}^{PY} is, for $D = 5$, also marginally better than Z_{BC}, and both compare well with the empirical Z_{ASV}.

3 DISCUSSION

The CS-like EOS lead to results for the hard D-spheres which compare extremely well with the available MD results, even though the virial and compressibility EOS from which they are deduced worsen with increasing dimensionality. Moreover, the results are of similar accuracy as those obtained by Baus and Colot[5]. We believe that our prescription has the advantage in that it does not require the evaluation of virial coeffecients nor a guess on how many of them are needed to produce the best results.

The success of the CS-like EOS suggests that a Verlet–Weis[10]-like prescription for all hard D-spheres may also meet with similar success in describing the pair

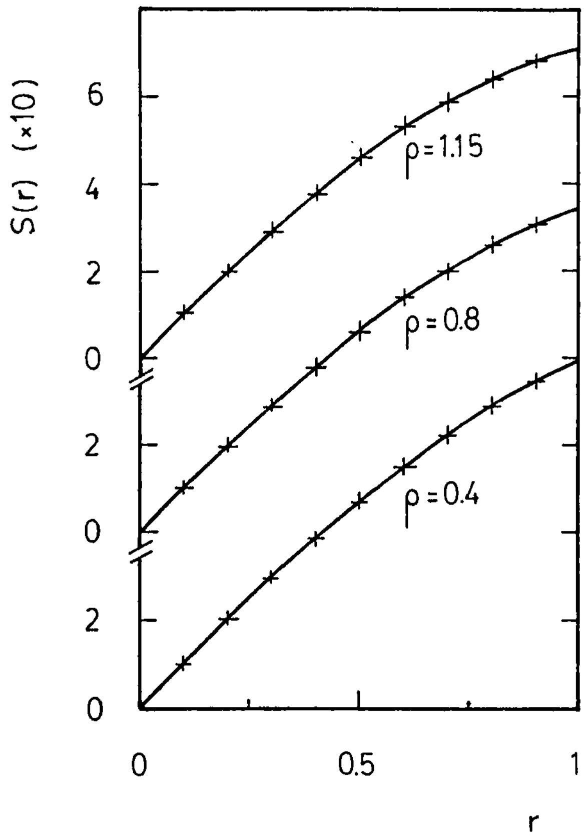

Figure 2 The correlation function $S(r)$ for hard hyperspheres, $D = 5$, at three values of the reduced density, $\rho = 0.4$, 0.8 and 1.15. The continuous curves are the results from Leutheusser's ansatz (Eq. 2.20); the crosses denote the results from the analytical solution of the PY equation.

distribution function $g(r)$. Work on this problem is being actively pursued and will be reported on completion.

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