Thermodynamics and structure of a fluid of hard rods, disks, spheres, or hyperspheres from rescaled virial expansions

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By rescaling the exact low-density results practical expressions are obtained for the equation of state and the direct correlation function of a fluid of hard D-spheres allowing a unified treatment of both the odd and even space dimensionalities D. The accuracy of these results is tested against those of the current literature and found to be excellent, in particular for hard disks ($D=2$), whereas the hard-rod results ($D=1$) are reproduced exactly.

I. INTRODUCTION

In the high-density region the behavior of a fluid (liquid or vapor) is dominated by the excluded-volume effects associated with the hard cores of its constituents. It is therefore quite natural to study model fluids with only hard cores and no interatomic attractions. Computer simulations have shown[1] that such fluids exhibit indeed many liquidlike properties. Nowadays the theoretical studies of liquids[1] use almost invariably some hard-core reference fluid as basis for a perturbation expansion of the properties of more realistic liquids. The most widely used hard-core reference fluid in D dimensions is certainly the fluid of hard D-spheres. It is surprising, however, that whereas the properties of a fluid of hard rods ($D=1$) are known exactly,[2] not a single exact result is known when $D\neq 1$. One therefore usually resorts to some approximate integral equation for the structural functions (from which the thermodynamics can then be obtained as a byproduct) and compares their numerical solution to the results of computer simulations. For the hard D-sphere systems under consideration the Percus-Yevick (PY) equations[1] have played a particular role since for $D=1$ and 3 they can be solved analytically[1] while the results compare also favorably (except for the thermodynamic inconsistency between the $D=3$ virial and compressibility equations of state) with the computer simulation results. Unfortunately the PY equations cannot be solved analytically for the *even* values of D, including the widely studied hard-disk system ($D=2$). Many pieces of knowledge combining the results of computer simulations, numerical solutions, and analytic approximations are scattered in the literature but none of them allows a parallel treatment of different D values, especially of odd and even D values.

It is the purpose of the present investigation to derive unified expressions for hard D-spheres, with a generic D dependence and an accuracy comparable to that of the current literature. The emphasis here will not be so much on the solution of the underlying theoretical problems but instead on the construction of practical algorithms. A preliminary account[3] and a first application[4] have already been presented elsewhere.

In Sec. II we present our results for the equation of state which are then used in Sec. III to construct the corresponding structural data. Some conclusions are gathered in the final Sec. IV while the Appendixes A–C contain some more mathematical material.

II. THE THERMODYNAMICS OF A FLUID OF HARD D-SPHERES

We consider a D-dimensional system of D-dimensional spheres of diameter σ with an infinitely steep repulsive pair potential $V(|\mathbf{r}|)$, $V(|\mathbf{r}|)=\infty$ for $|\mathbf{r}|<\sigma$ and $V(|\mathbf{r}|)=0$ for $|\mathbf{r}|\geq\sigma$, where $|\mathbf{r}|$ denotes the D-dimensional distance (for notational convenience the D dependence will not always be explicitly indicated). The average number density of D-spheres is ρ and η is the corresponding packing fraction, i.e., the fraction of the total volume occupied by the D-spheres. The general relation between ρ and η reads

$$\eta=V_D\left[\frac{\sigma}{2}\right]^D\rho=\frac{\pi^{D/2}\sigma^D}{2^D\Gamma(1+D/2)}\rho\ , \tag{2.1}$$

where $\Gamma(1+z)=z!$ is the Γ function. In Eq. (2.1) we took into account that in D-space the volume of a sphere of unit radius is $V_D=\pi^{D/2}/\Gamma(1+D/2)$, whereas $S_D=DV_D$ is its surface area. The central thermodynamic quantity is the compressibility factor, $Z=\beta p/\rho$, i.e., the dimensionless combination of the density (ρ), the pressure (p), and the temperature ($\beta=1/k_BT$), which for hard D-spheres depends only on the density $Z=Z(\eta)$. From $Z(\eta)$ we can compute the isothermal compressibility χ_T, the free energy per particle f/ρ (f being the free energy per unit volume), and the constant pressure specific heat per particle c_p as

$$\frac{\beta p}{\rho}=Z(\eta),\quad \beta\left[\frac{\partial p}{\partial\rho}\right]_T=\frac{\beta}{\rho\chi_T}=\frac{\partial}{\partial\eta}[\eta Z(\eta)]\ , \tag{2.2a}$$

$$\frac{\beta f}{\rho}=\ln\left[\left[\frac{\lambda}{\sigma}\right]^D 2^D\Gamma(1+D/2)\pi^{-D/2}\right]+\ln\eta-1+\int_0^\eta d\eta'\,\frac{Z(\eta')-1}{\eta'}\ , \tag{2.2b}$$

$$\frac{c_p}{k_B}=\frac{D}{2}+\frac{[Z(\eta)]^2}{\frac{\partial}{\partial\eta}[\eta Z(\eta)]}\ , \tag{2.2c}$$

where in Eq. (2.2b) the first term [involving the thermal de Broglie wavelength $\lambda=h(2\pi m k_B T)^{-1/2}$] is the purely kinetic contribution which is independent of the density.

For *low* densities the central quantity, $Z(\eta)$, can be expanded into a virial series,

$$Z(\eta)=1+\sum_{n=1}^{\infty} b_n \eta^n\ , \tag{2.3}$$

with expansion coefficients b_n related to the standard[1] virial coefficients B_n by

$$b_n\eta^n=B_{n+1}\rho^n,\quad b_n=2^{(D-1)n}\frac{B_{n+1}}{(B_2)^n}\ , \tag{2.4}$$

where B_2 equals one-half the volume of a sphere of *radius* σ,

$$B_2=\tfrac{1}{2}V_D\sigma^D=\pi^{D/2}\sigma^D/2\Gamma(1+D/2)\ . \tag{2.5}$$

The computation of B_3 for general D is already nonelementary. Luban and Baram[5] have given a series representation of B_3 while in Appendix A we derive the equivalent but more compact result

$$\frac{B_3}{(B_2)^2}=2\omega_D(\tfrac{1}{2})\equiv 2I_{3/4}((D+1)/2,\tfrac{1}{2})\ , \tag{2.6}$$

where $\omega_D(x)\equiv I_{1-x^2}((D+1)/2,\tfrac{1}{2})$ is an auxiliary function (which will be used repeatedly in Sec. III) related to the normalized incomplete beta function $I_x(a,b)$ [see (A6)–(A13)]. The third virial coefficient B_3 can then be obtained most easily from (2.5) and (2.6) and the following recurrence relation [see (A10)],

$$I_{3/4}((D+1)/2,\tfrac{1}{2})=I_{3/4}((D-1)/2,\tfrac{1}{2}) - \frac{3^{(D-1)/2}\Gamma(D/2)}{2^D\Gamma(\tfrac{1}{2})\Gamma((D+1)/2)}\ , \tag{2.7}$$

TABLE I. Some exact results for the expansion coefficients used in Eqs. (2.3) and (2.11) as obtained from Eqs. (2.5)–(2.8) and Eqs. (2.12)–(2.17).

D	2	3	4	5
$\frac{B_3}{(B_2)^2}$	$\frac{4}{3}-\frac{\sqrt{3}}{\pi}$	$\frac{5}{8}$	$\frac{4}{3}-\frac{3\sqrt{3}}{2\pi}$	$\frac{53}{128}$
b_2	$\frac{16}{3}-\frac{4\sqrt{3}}{\pi}$	10	$\frac{256}{3}-\frac{96\sqrt{3}}{\pi}$	106
c_1	0	1	4	11
c_2	$\frac{7}{3}-\frac{4\sqrt{3}}{\pi}$	1	$\frac{178}{3}-\frac{96\sqrt{3}}{\pi}$	36

starting from [see (A12) and (A13)]

$$I_{3/2}(\tfrac{1}{2},\tfrac{1}{2})=\tfrac{2}{3},\quad I_{3/4}(1,\tfrac{1}{2})=\tfrac{1}{2} \tag{2.8}$$

for, respectively, $D=0$ and $D=1$. Some explicit results for B_3 can be found in Table I. Except for the following two particular cases,[6,7]

$$\frac{B_4}{(B_2)^3}=\begin{cases} 2-\dfrac{9\sqrt{3}}{2\pi}+\dfrac{10}{\pi^2}, & D=2 \quad (2.9)\\[2ex] \dfrac{219\sqrt{2}}{2240\pi}+\dfrac{4131}{2240}\pi\arccos\dfrac{1}{\sqrt{3}}-\dfrac{89}{280}, & D=3 \end{cases} \tag{2.10}$$

the higher virial coefficients B_n $(n>3)$ can no longer be obtained analytically but some of them have been evaluated by numerical integration[8–13] (up to $n=7$ for $D=2$ and 3 and up to $D=9$ for $n=4$). All results known to us are given in Table II [not included, however, is the trivial $D=1$ case for which $B_{n+1}=(B_2)^n=\sigma^n$ for all n].

For the *high* densities relevant to the liquid phase the slowly convergent virial series (2.3) cannot be used, but the knowledge of the virial coefficients of Table II can be exploited in various series convergence accelerating

TABLE II. All the known virial coefficients for hard D-spheres. The dots indicate that the corresponding number is known exactly.

	$B_3/(B_2)^2$	$B_4/(B_2)^3$	$B_5/(B_2)^4$	$B_6/(B_2)^5$	$B_7/(B_2)^6$
$D=2$	0.7820. . . [a]	0.5322. . . [b]	0.333 556 04[c]	0.198 83[c]	0.1148[c]
$D=3$	0.625[a]	0.2869[d]	0.110 252[e]	0.0389[e]	0.0137[e]
$D=4$	0.5063. . . [a]	0.1513[f]			
$D=5$	0.4140. . . [a]	0.0746[g]	0.0148[g]		
$D=6$	0.3409. . . [a]	0.0328[h]			
$D=7$	0.2822. . . [a]	0.0098[h]			
$D=8$	0.2346. . . [a]	−0.0026[h]			
$D=9$	0.1957. . . [a]	−0.0084[h]			

[a]Source, from Eq. (2.6).
[b]Source, from Eq. (2.9).
[c]Source, from Ref. 9.
[d]Source, from Eq. (2.10).
[e]Source, from Ref. 10.
[f]Source, from Ref. 13.
[g]Source, from Ref. 12.
[h]Source, from Ref. 11.

methods. The exact radius of convergence of the virial series (2.3) is still unknown although often quoted candidates are the densities of random and of crystal close packing.[14] Approximate theories, however, cannot account for close-packing effects and usually lead to virial series with a singularity at $\eta=1$. Since D-spheres are not space filling (except for $D=1$), this corresponds to a physically unattainable density and hence $\eta=1$ can represent only an upper bound for the radius of convergence of the virial series. Nevertheless, in order to maintain contact with the well-known approximate theories, it is of practical interest to keep the singularity at $\eta=1$. We therefore propose to *rescale* the virial series (2.3) by writing the density expansion of $Z(\eta)$ as

$$Z(\eta)=\frac{1+\sum_{n=1}^{\infty} c_n \eta^n}{(1-\eta)^D}, \tag{2.11}$$

where the strength of the singularity at $\eta=1$ $[\propto(1-\eta)^{-D}]$ is inspired by the results of scaled particle theory (SPT).[1] Equation (2.11) has an interesting generic structure with respect to D and contains no adjustable parameters. As we now show it also leads to simple and accurate equations of state for all D values.

It is an easy matter to relate the new expansion coefficients c_n of (2.11) to the virial coefficients b_n of (2.3). The general result is

$$c_n=\sum_{p=0}^{D} \frac{(-1)^p D!}{(D-p)!p!} b_{n-p}, \tag{2.12}$$

where it is understood that $b_n=0$ when $n<0$ and $b_0=1$. It is seen from (2.12) that each c_n involves only those b_p (or B_{p+1}) with $p \leq n$. For instance we have

$$c_1=2^{D-1}-D, \tag{2.13}$$

$$c_2=\tfrac{1}{2}D(D-1)-D2^{D-1}+4^{D-1}\frac{B_3}{(B_2)^2}, \tag{2.14}$$

etc, for general D or

$$c_n=\begin{cases} b_n-b_{n-1}, & D=1 \quad (2.15)\\ b_n-2b_{n-1}+b_{n-2}, & D=2 \quad (2.16)\\ b_n-3b_{n-1}+3b_{n-2}-b_{n-3}, & D=3 \quad (2.17)\end{cases}$$

etc, for general n. Some explicit c_n values are given in Tables I and III.

In practice, the infinite series (2.3) and (2.11) have to be truncated at some finite order N, bound by the number of known virial coefficients (see Table II). As a result $Z(\eta)$ will be approximated by $Z_N(\eta)$,

$$Z_N(\eta)=\frac{1+\sum_{n=1}^{N} c_n \eta^n}{(1-\eta)^D}, \tag{2.18}$$

whose virial expansion is identical to that of (2.3) up to the term b_N included. It is also possible to compute $Z_N(\eta)$ iteratively from

$$Z_N(\eta)=Z_{N-1}(\eta)+c_N\eta^N(1-\eta)^{-D}, \quad Z_0(\eta)=(1-\eta)^{-D} \tag{2.19}$$

when a new coefficient b_N (and hence c_N) is added to those already retained. As seen from (2.18) our proposal for $Z_N(\eta)$ has the form of a particular Padé approximation $[P_N(\eta)/Q_D(\eta)$ with $Q_D(\eta)\equiv(1-\eta)^D]$ and it is hence obvious that for a particular value of D and N it is always possible to construct Padé approximations more accurate than $Z_N(\eta)$. Equation (2.18) has, however, the following interesting properties: (i) to be generic with respect to D (ii) to lead to accurate equations of state for each D, and (iii) to yield equations which become more accurate when N is increased, certainly at low density but also (although not uniformly) at high density. We now consider some explicit results.

A. Hard rods ($D=1$)

For hard rods ($\eta=\sigma\rho, B_2=\sigma$) the equation of state is known exactly,[2]

$$Z(\eta)=\frac{1}{(1-\eta)}, \tag{2.20}$$

i.e., $b_n=1$ for all $n \geq 1$. Substituting $b_n=1$ into (2.12) we find [see (2.15)] $c_n=0$ ($n \geq 1$) and $Z_N(\eta)$ of (2.18) reduces [see (2.19)] to the exact result (2.20) whatever the value of N. Our proposal is thus exact for $D=1$ as are also the results[1] of the PY and SPT equations for this particular dimensionality.

B. Hard disks ($D=2$)

In this important case ($\eta=\pi\sigma^2\rho/4$, $B_2=\pi\sigma^2/2$), no exact results are available but many empirical proposals have been formulated. Most of them are of the type

$$Z(\eta)=\frac{1+a\eta^2}{(1-\eta)^2}-\frac{b\eta^{3+c}}{(1-\eta)^{2+d}}, \tag{2.21}$$

TABLE III. The expansion coefficients used in (2.18) as obtained from (2.12)–(2.17) and the virial coefficients of Table II. For convenience only five digits have been displayed.

	c_1	c_2	c_3	c_4	c_5	c_6
$D=1$	0	0	0	0	0	0
$D=2$	0	0.1280	0.0018	−0.0507	−0.0533	−0.0410
$D=3$	1	1	−0.6352	−0.8697	0.2543	2.9231
$D=4$	4	6.4057	−8.1170			
$D=5$	11	36	−74.438	347.12		

with specific values for the constants a, b, c, and d. Starting from the results of SPT (Ref. 15) ($a=0=b$), Henderson[16] ($b=0$, $a=0.125$) and Kratky[8(b)] ($b=0$, $a=0.112$) have proposed a first modification thereof which yields somewhat too small pressures at low densities (because the third virial coefficient B_3 is not reproduced exactly) and somewhat too large pressures at high density. A second modification ($b\neq 0$) by Henderson[17] ($a=0.128$, $b=0.043$, $c=1=d$), Kratky[8(b)] ($a=0.12802$, $b=0.03003$, $c=0$, $d=1$), and Verlet and Levesque[19] ($a=0.125$, $b=2^{-5}$, $c=1$, $d=2$) corrects for the low-density behavior but has the somewhat unpleasant feature to lead to negative pressures at very high densities (in the metastable fluid region). In Table IV we compare our results, $Z_N(\eta)$ of (2.18), with the recent very accurate Monte Carlo–molecular-dynamics (MC–MD) computer simulation results of Erpenbeck and Luban.[9] It is seen there that $Z_0(\eta)$ (which is identical to the result of SPT) and $Z_2(\eta)$ are bracketing the simulation results whereas $Z_6(\eta)$ is coming very close to it. Our proposal is also more accurate than the results obtained from the integral equations of PY,[18] of Lado,[18] and of Verlet and Levesque.[19] Only some of the more sophisticated Padé approximations[8,9] and those approximations containing adjustable parameters[17] can compete with $Z_6(\eta)$. An overall view of the various results in the high-density region is given in Fig. 1. It is seen there that our simple proposal (without adjustable parameters) is in excellent agreement with the simulation results[9] (the maximum deviation reaching half a percent only at the highest density considered in the simulations).

C. Hard spheres ($D=3$)

For this well-known case ($\eta=\pi\sigma^3\rho/6$, $B_2=2\pi\sigma^3/3$) some of the approximate theories (such as PY and SPT) can be solved exactly while some very accurate empirical equations of state have also been elaborated. All of these results are of the general form

$$Z(\eta)=\frac{1+\eta+\eta^2-a\eta^3-b\eta^4}{(1-\eta)^3}\ , \tag{2.22}$$

which is again compatible with (2.18). Equation (2.22) contains the results of SPT (Ref. 15) ($a=0=b$), of the PY compressibility ($a=0=b$) and virial ($a=3, b=0$) equations,[1] the Carnahan-Starling equation[1] ($a=1$, $b=0$), and the recent proposal of Kolafa quoted by Boublik[20] ($a=\frac{2}{3}=b$). Considering $Z_N(\eta)$ of (2.18) we observe that $Z_2(\eta)$ is identical to the result of SPT whereas $Z_4(\eta)$ is very close to the proposal of Kolafa which itself is slightly better than the Carnahan-Starling result when compared to the recent (MC–MD) simulation results of Erpenbeck and Wood.[21] In the present case $Z_6(\eta)$ is less good than $Z_4(\eta)$ but still much better than $Z_2(\eta)$ which is identical to the widely used PY compressibility equation of state. Details are displayed in Table V and Fig. 2.

D. Hard hyperspheres ($D=4$)

No theoretical results whatsoever are known to us for this case ($\eta=\pi^2\sigma^4\rho/32$, $B_2=\pi^2\sigma^4/4$). Our results for $Z_N(\eta)$ of (2.18) are compared to the MD simulation results of Michels and Trappeniers[22] in Table VI and Fig. 3. It is seen that Z_3 (which exhaust the known virial coefficients) compares well with the simulation results.

E. Hard hyperspheres ($D=5$)

For this case ($\eta=\pi^2\sigma^5\rho/60$, $B_2=4\pi^2\sigma^5/15$) the PY equations have been solved analytically by Freasier and Isbister[12] and also by Leutheusser.[23] The result for the virial (v) and compressibility (c) equation of state can be written as

$$Z_{\text{PY-}v}(\eta)=1-32\eta Q_0(\eta)\ , \tag{2.23}$$

$$Z_{\text{PY-}c}(\eta)=\frac{1}{\eta}\int_0^\eta d\eta'[8Q_2(\eta')]^2\ , \tag{2.24}$$

where [using the notation of Eq. (3.37) below] Q_0 and Q_2 are defined

$$Q_0(\eta)=\frac{1}{120\eta(1-\eta)^3}[1-33\eta-87\eta^2-6\eta^3 -(1+18\eta+6\eta^2)^{3/2}]\ , \tag{2.25}$$

TABLE IV. The compressibility factor $Z_N(\eta)$ as obtained from (2.18) for hard disks ($D=2$) for $N=0,2$, and 6, compared to the very precise MC–MD data of Erpenbeck and Luban,[9] Z_{EL}, as a function of η_{cp}/η with $\eta_{cp}=0.9068\ldots$, the packing fraction at close packing ($\eta_{cp}=\pi/2\sqrt{3}$). The expression for Z_0 is identical to the result of SPT,[15] expression Z_2 was used in the freezing theory considered elsewhere[4] whereas Z_6 which involves seven virial coefficients comes very close to Z_{EL}. Notice also the convergence with respect to N: $Z_2\geq Z_6\geq Z_{\text{EL}}\geq Z_0$.

η_{cp}/η	Z_{EL}	Z_6	Z_2	Z_0
30	1.063 37	1.063 44	1.063 44	1.063 31
20	1.097 43	1.097 54	1.097 54	1.097 25
10	1.210 68	1.210 68	1.210 69	1.209 41
5	1.4983	1.498 42	1.498 51	1.492 22
3	2.0771	2.077 21	2.078 32	2.054 29
2	3.4243	3.424 52	3.435 76	3.347 64
1.8	4.1715	4.171 93	4.194 04	4.062 04
1.6	5.4963	5.498 13	5.548 20	5.329 02
1.5	6.6074	6.614 33	6.695 57	6.396 26
1.4	8.306	8.352 33	8.493 96	8.060 93

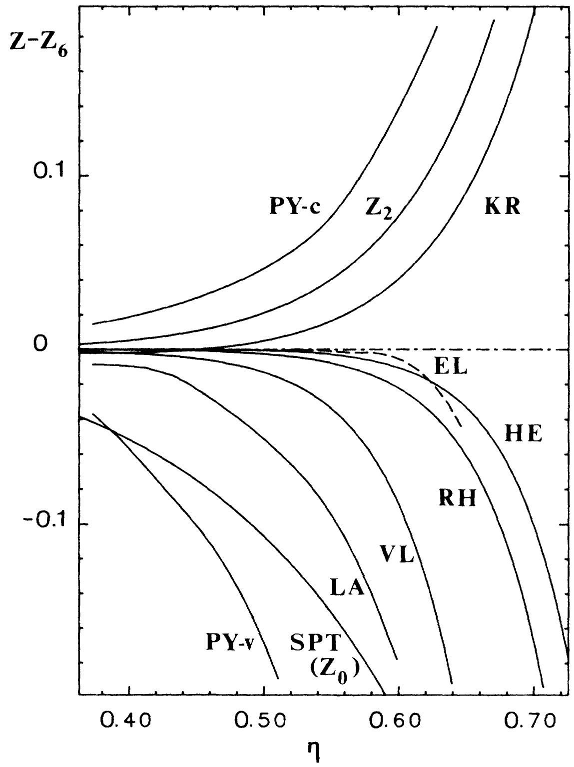

FIG. 1. The relative deviation, $Z - Z_6$, of the compressibility factor $Z(\eta)$ for hard disks ($D=2$) computed from various proposals compared to $Z_6(\eta)$ obtained from (2.18) as a function of η, for large densities (up to 20% below close packing; $\eta_{cp} \cong 0.91$). The curves are labeled as follows: EL corresponds to the simulation results of Erpenbeck and Luban (Ref. 9) (with error bars comparable to the line thickness); RH to the $P(3/3)$ Padé approximation of Ree and Hoover [Ref. 8(a)]; HE to (2.18) with $c=1=d$, $a=0.128$, and $b=0.043$ (fit) as proposed by Henderson (Ref. 17); KR to (2.18) with $b=0$ and $a=0.112$ (fit) as proposed by Kratky [Ref. 8(a)]; VL to (2.18) with $a=0.125$, $b=2^{-5}$, $c=1$, and $d=2$ as proposed by Verlet and Levesque (Ref. 19); LA to the pressure consistent integral equation of Lado (Ref. 18); PY-$c(v)$ to the compressibility (virial) equation of state resulting from the numerical solution of the PY equation (Ref. 18); SPT to the result of the scaled particle theory (Ref. 15); Z_0, Z_2 to the result of (2.18).

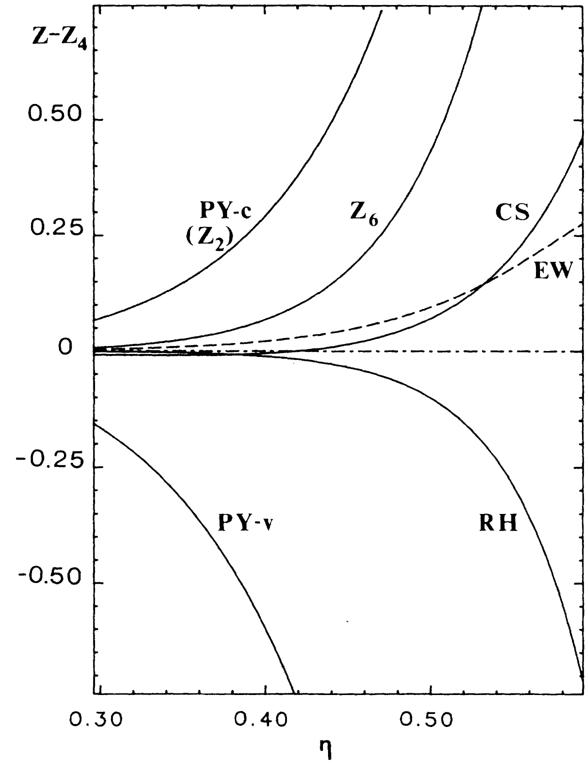

FIG. 2. The relative deviation, $Z - Z_4$, of the compressibility factor Z for hard spheres ($D=3$) computed from various proposals compared to Z_4 obtained from (2.18) as a function of η for large densities (up to 20% below close packing; $\eta_{cp} \cong 0.74$). The curves are labeled as follows: EW corresponds to the simulation results of Erpenbeck and Wood (Ref. 21) (with error bars comparable to the line thickness); CS to (2.22) with $a=1$ and $b=0$ as proposed by Carnahan and Starling; (Ref. 1) RH to the $P(3/3)$ Padé approximation of Ree and Hoover [Ref. 8(a)]; PY-$c(v)$ to the compressibility (virial) equation of state of the PY theory (Ref. 1); Z_6 to the results of (2.18).

TABLE V. The compressibility factor $Z_N(\eta)$ as obtained from (2.18) for hard spheres ($D=3$) for $N=2$, 4, and 6, compared to the recent MC–MD simulations of Erpenbeck and Wood,[21] $Z_{\rm EW}$, as a function of η_{cp}/η with $\eta_{cp}=\pi/3\sqrt{2}=0.7404\ldots$. The expression for Z_2 is identical to the SPT or PY-c results[1] while Z_4 is close to the simulation results ($Z_2 \geq Z_{\rm EW} \geq Z_4$) and Z_6 is crossing $Z_{\rm EW}$.

η_{cp}/η	$Z_{\rm EW}$	Z_6	Z_4	Z_2
25	1.127 75	1.127 750	1.127 750	1.127 769
18	1.182 84	1.182 839	1.182 839	1.182 892
10	1.359 44	1.359 427	1.359 426	1.359 784
5	1.888 57	1.888 516	1.888 437	1.892 451
4	2.244 52	2.244 506	2.244 186	2.253 521
3	3.032 23	3.033 017	3.030 924	3.060 838
2	5.853 51	5.877 755	5.840 523	6.035 041
1.8	7.436 69	7.495 420	7.411 257	7.750 244
1.7	8.610 01	8.706 121	8.572 913	9.038 990
1.6	10.209 66	10.373 926	10.153 819	10.817 372

$$Q_2(\eta)=-\frac{(1+18\eta+6\eta^2)^{1/2}}{24(1-\eta)^3}[2+3\eta+(1+18\eta+6\eta^2)^{1/2}]\ . \tag{2.26}$$

The thermodynamic inconsistency between (2.23) and (2.24) is worse[12] here than for the lower D values. Notice that as $\eta\to 1$ we have from (2.24) $Z_{\text{PY-}c}\propto(1-\eta)^{-5}$ in agreement with our assumption (2.18). Comparing our results for $Z_N(\eta)$ of (2.18) to the (MD) simulation results of Michels and Trappeniers[22] we find (see Table VII and Fig. 4) that $Z_4(\eta)$ (which exhausts the known virial coefficients) is almost identical to (but slightly better than) $Z_{\text{PY-}c}$ and in fair agreement with the simulation results whereas $Z_{\text{PY-}v}$ largely underestimates $Z(\eta)$.

F. Summary

No simulation results are known to us for $D>5$ and it becomes hence difficult to test our general proposal (2.18) for larger D values. The information gathered thus far ($1\le D\le 5$) seems to indicate, however, that the assumed behavior $[Z(\eta)\propto(1-\eta)^{-D}]$ for the rescaled virial expansion of (2.11), although presumably not exact (except for $D=1$), provides a reasonable generic ansatz for constructing fairly accurate approximate equations of state (without adjustable parameters) for fluids of hard D-spheres whatever the value of D. The general trend with respect to D is illustrated in Fig. 5.

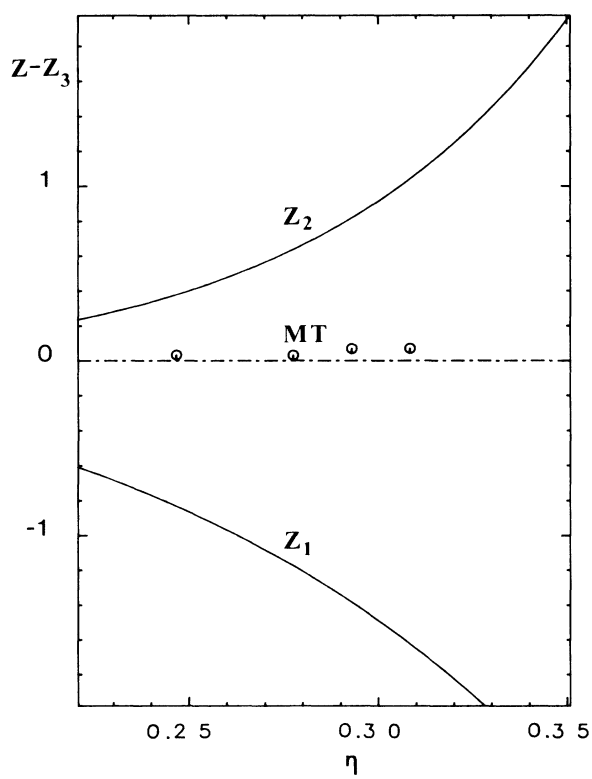

FIG. 3. The relative deviation, $Z-Z_3$, of the compressibility factor Z for hard hyperspheres ($D=4$) computed from various proposals compared to Z_3 obtained from (2.18) as a function of η for large densities (up to 40% below close packing; $\eta_{cp}\cong 0.55$). The curves are labeled as follows: MT corresponds to the simulation results of Michels and Trappeniers (Ref. 22); Z_1 and Z_2 correspond to (2.18).

TABLE VI. The compressibility factor $Z_N(\eta)$ as obtained from (2.18) for hard hyperspheres ($D=4$) for $N=1,2,3$, compared to the MD simulation results of Michels and Trappeniers,[22] Z_{MT} as a function of $\rho\sigma^4$. It is seen that $Z_1\le Z_3\le Z_{\text{MT}}\le Z_2$ with Z_3 (which exhausts the known virial coefficients) close to Z_{MT}.

$\rho\sigma^4$	Z_{MT}	Z_3	Z_2	Z_1
0.20	1.637	1.6373	1.6397	1.6083
0.40	2.670	2.6682	2.6940	2.5289
0.60	4.335	4.3261	4.4427	3.9454
0.80	7.038	7.0043	7.3831	6.1717
0.90	8.955	8.9229	9.5603	7.7481
0.95	10.147	10.0774	10.8946	8.6935
1.00	11.458	11.3876	12.4287	9.7649

III. THE STRUCTURE OF A FLUID OF HARD D-SPHERES

The structural functions which will be considered here consist of the DCF (direct correlation function), $c(x;\eta)$, and the related static structure factor $S(q;\eta)=[1-c(q;\eta)]^{-1}$, with $c(q;\eta)$ the spatial Fourier transform of $\rho c(x;\eta)$. For hard D-spheres these quantities do not depend on the temperature but only on the density ρ through the dimensionless packing fraction η while it is also convenient to introduce a dimensionless distance $x=|\mathbf{r}|/\sigma$ and a dimensionless wave number $q=|\mathbf{k}|\sigma$. These structural functions are related to the thermodynamics of Sec. II through the compressibility equation of state

$$\beta\frac{\partial p}{\partial\rho}=1-c(q=0;\eta)\equiv 1-D\,2^D\eta\int_0^\infty dx\, x^{D-1}c(x;\eta) \tag{3.1}$$

TABLE VII. The compressibility factor $Z_N(\eta)$ as obtained from (2.18) for hard hyperspheres ($D=5$) for $N=2,3,4$, compared to the MD simulation results of Michels and Trappeniers,[22] Z_{MT} as a function of $\rho\sigma^5$. It is seen that $Z_2\ge Z_4\ge Z_{\text{MT}}\ge Z_3$ with Z_3 close to Z_{MT}.

$\rho\sigma^5$	Z_{MT}	Z_4	Z_3	Z_2
0.20	1.653	1.6532	1.6527	1.6558
0.40	2.624	2.6209	2.6117	2.6415
0.60	4.008	4.0312	3.9758	4.0961
0.80	5.997	6.0854	5.8746	6.2181
1.00	8.748	9.1032	8.4790	9.2927
1.10	10.523	11.1231	10.1136	11.3100
1.15	11.589	12.2967	11.0284	12.4661
1.18	12.217	13.0606	11.6111	13.2125

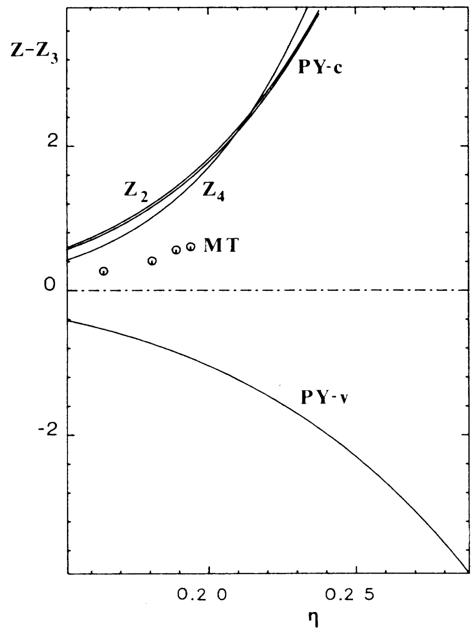

FIG. 4. The relative deviation, $Z - Z_3$, of the compressibility factor Z for hard hyperspheres ($D=5$) computed from various proposals and compared to Z_3 obtained from (2.18) as a function of η for large densities (up to 25% below close packing; $\eta_{cp} \cong 0.38$). The curves are labeled as follows: MT corresponds to the simulation results of Michels and Trappeniers (Ref. 22); Y-c to the PY compressibility equation (2.23); PY-v to the PY virial equation (2.24); Z_2 and Z_4 to the results of (2.18).

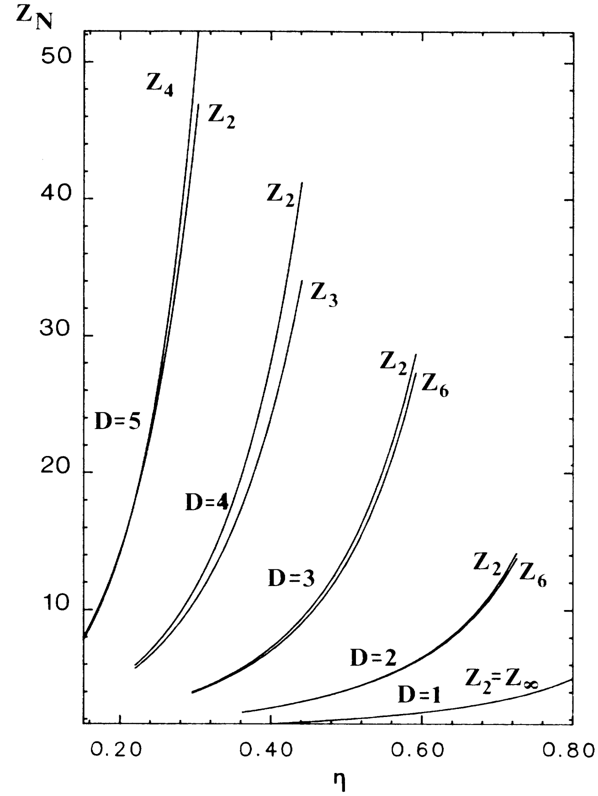

FIG. 5. The value of the compressibility factor Z for hard D-spheres ($1 \leq D \leq 5$) as obtained from $Z_N(\eta)$ of (2.18) with N corresponding for each D to the number of known virial coefficients and also for $N=2$ as a function of η for densities ranging from zero up to 10% below the close-packing density of the corresponding D value.

and the virial equation of state, which for hard D-spheres can be written as

$$\frac{\beta p}{\rho} = 1 + 2^{D-1}\eta[c(x=1_+;\eta) - c(x=1_-;\eta)] \ . \quad (3.2)$$

The problem of finding an explicit expression for $c(x;\eta)$ consistent with both (3.1) and (3.2) is still an unsolved one for $D \neq 1$. Usually one has to accept some thermodynamic inconsistency between the results derived from (3.1) and those obtained from (3.2) unless consistency is imposed by some *ad hoc* procedure. Even when accepting some amount of thermodynamic inconsistency, the explicit determination of $c(x;\eta)$ remains a difficult problem because many different analytic forms of $c(x;\eta)$ will in general be compatible with the same thermodynamics. The merits of the PY approximation[1] cannot be underscored in this respect since it gives a good representation of both $c(x;\eta)$ and of the thermodynamics $Z(\eta)$ [at least via the compressibility route (3.1)]. Unfortunately, the PY equations can be solved analytically [for $c(x;\eta)$] only for the odd values of D (excluding the interesting hard-disk case) provided moreover that D is not too large[23] (for $D \geq 7$ one runs into intractable algebraic equations). Therefore we will again look[3] for a practical ansatz for $c(x;\eta)$ which, although inspired by the PY approximation, is simpler to handle for any D, odd or even. We first observe that the Ornstein-Zernike equation[1] relating $c(x;\eta)$ to the pair correlation function $g(x;\eta)$ can be written at $x=0$ as

$$c(x=0;\eta) = g(x=0;\eta) - 1 - \rho \int d\mathbf{r}\, c(x,\eta)[g(x;\eta)-1]$$
$$\equiv -[1-c(q=0;\eta)] - \rho \int d\mathbf{r}\, c(x;\eta) g(x;\eta) \quad (3.3)$$

since $g(x=0;\eta)=0$. If, moreover, the overlap integral between $g(x;\eta)$ and $c(x;\eta)$ is small (or strictly zero as assumed in the PY approximation for hard D-spheres), the last term on the right-hand side of (3.3) can be neglected and we obtain using (3.1) and (2.2a)

$$-c(x=0;\eta) = 1 - c(q=;\eta) = \beta \frac{\partial p}{\partial \rho} = \frac{\partial}{\partial \eta}[\eta Z(\eta)] \ . \quad (3.4)$$

From (3.4) we deduce that the overall scale of $c(x;\eta)$, which is set by $c(x=0;\eta)$, is determined by the inverse of the isothermal compressibility χ_T of (2.2a) which can be obtained from the approximation (2.18) to $Z(\eta)$ proposed in Sec. II. To find the spatial structure of $c(x;\eta)$ it will hence suffice to consider the rescaled DCF

$c(x;\eta)/c(x=0;\eta)$. For the latter quantity we find at *low* density

$$\frac{c(x;\eta)}{c(x=0;\eta)}=\begin{cases}1-2^D\eta+2^D\eta\omega_D(x/2)\,, & x\le 1\\ 0, & x>1\end{cases} \tag{3.5}$$

where $\omega_D(x)$ is the overlap volume of two D-spheres of diameter σ whose centers are a distance $x=|\mathbf{r}|/\sigma$ apart divided by the volume of one of the spheres,

$$\omega_D(x)=\frac{\int d\mathbf{r}'\,\Theta(\sigma/2-|\mathbf{r}'|)\Theta(\sigma/2-|\mathbf{r}-\mathbf{r}'|)}{\int d\mathbf{r}''\,\Theta(\sigma/2-|\mathbf{r}''|)}\,, \tag{3.6}$$

with $\Theta(x)$ the Heaviside unit step function [$\Theta(x)=1$ if $x\ge 0$ and zero otherwise]. To complete our construction of $c(x;\eta)$ we now assume that, at any density, the structure of the low-density result (3.5) remains correct if reformulated in terms of a rescaled density-dependent diameter σ',

$$\frac{c(x;\eta)}{c(x=0;\eta)}=\begin{cases}1-\eta'+\eta'\omega_D(x')\,, & x\le 1\\ 0\,, & x>1\end{cases} \tag{3.7}$$

where η' and x' are the rescaled variables: $\eta'=\eta a^D$ and $x'=x/a$ with $a=a(\eta)$ being the ratio, $a=\sigma'/\sigma$, of the effective to the real diameter.

As such, our proposal (3.7) contains two unknown scaling functions, $a=a(\eta)$ and $c(x=0;\eta)$, and one relation (3.4). It is possible to find a second relation[3,24] but this usually leads to complicated algebraic equations. We found it much more practical to rewrite (3.4) as

$$c(x=0;\eta)=-\frac{\partial}{\partial\eta}[\eta Z(\eta)]\,, \tag{3.8}$$

$$1-c(q=0;\eta)=\frac{\partial}{\partial\eta}[\eta Z(\eta)]\,, \tag{3.9}$$

and to impose the equation of state, $Z=Z(\eta)$, to be used in (3.8) and (3.9), for instance by approximating $Z(\eta)$ by $Z_N(\eta)$ of Sec. II. Given $Z(\eta)$, Eq. (3.8) fixes $c(x=0;\eta)$ whereas Eq. (3.9) fixes the remaining scaling function $a=a(\eta)$. As a result of (3.8) and (3.9) the compressibility equation of state (3.1) underlying our ansatz (3.7) will be identical to the imposed equation of state $Z(\eta)$.

Explicitly, we thus propose the following approximate expression for the DCF of a fluid of hard D-spheres:

$$c(x;\eta)=-\frac{\partial}{\partial\eta}[\eta Z(\eta)]\Theta(1-x)\times\left[1-a^D\eta+a^D\eta\omega_D\left[\frac{x}{a}\right]\right]\,, \tag{3.10}$$

where (i) the overlap integral $\omega_D(x)$ of (3.6) can be computed (see Appendix B) in terms of the normalized incomplete beta function [see (A6)]as

$$\omega_D(x)=I_{1-x^2}((D+1)/2,1/2) \tag{3.11}$$

or, more practically, from the recurrence relation [see (A10)–(A13)]

$$\omega_0(x)=\frac{2}{\pi}\arccos x\,, \tag{3.12}$$

$$\omega_1(x)=1-x\,, \tag{3.13}$$

$$\omega_D(x)=\omega_{D-2}(x)-x(1-x^2)^{(D-1)/2}\frac{\Gamma(D/2)}{\Gamma(\frac{1}{2})\Gamma((D+1)/2)}\quad(D\ge 2)\,, \tag{3.14}$$

for instance,

$$\omega_2(x)=\frac{2}{\pi}[\arccos x-x(1-x^2)^{1/2}]\,, \tag{3.15}$$

$$\omega_3(x)=1-\tfrac{3}{2}x+\tfrac{1}{2}x^3\,, \tag{3.16}$$

$$\omega_4(x)=\frac{2}{\pi}\left[\arccos x-\left[\frac{5}{3}x-\frac{2}{3}x^3\right](1-x^2)^{1/2}\right]\,, \tag{3.17}$$

$$\omega_5(x)=1-\tfrac{15}{8}x+\tfrac{5}{4}x^3-\tfrac{3}{8}x^5\,, \tag{3.18}$$

etc. (ii) the underlying equation of state, $Z=Z(\eta)$, will be approximated by $Z_N(\eta)$ of (2.18) (iii) the diameter rescaling, $a=a(\eta)$, will be determined, for a given $Z(\eta)$, from Eq. (3.9). To this end we first compute $c(q;\eta)$ (see Appendix C) as

$$c(q;\eta)=-\eta\frac{\partial}{\partial\eta}[\eta z(\eta)]((1-a^D\eta)2^Df_{D/2}(q)+a^D\eta\{[a^{D/2}f_{D/2}(aq/2)]^2+H_D(q;a)\}) \tag{3.19}$$

with

$$f_\nu(q)=\left[\frac{2}{q}\right]^\nu\Gamma(1+\nu)J_\nu(q) \tag{3.20}$$

an auxiliary function related to the Bessel function $J_\nu(q)$ and such that $f_\nu(q=0)=1$. In Eq. (3.19), $H_D(q;a)$ is a one-dimensional integral given by

$$H_D(q;a)=\frac{2^{D+1}}{B((D+1)/2,1/2)}\int_{1/a}^{1}dx(1-x^2)^{(D-1)/2}[f_{D/2}(q)-(ax)^Df_{D/2}(aqx)] \tag{3.21}$$

with $B(a,b)$ the beta function [see (A7)]. For general D, Eq. (3.21) has to be evaluated numerically in order to obtain the static structure factor via (3.19). Returning to (3.9) we obtain using (3.19) and separating the variables

$$a^D(a^D-2^D+H_D(q=0;a))=\eta^{-2}\left[1-2^D\eta-\left[\frac{\partial}{\partial\eta}[\eta Z(\eta)]\right]^{-1}\right]\,, \tag{3.22}$$

which is the equation determining a as a function of η, $a=a(\eta)$. The quantity $H_D(q=0;a)$, appearing in (3.22), can be obtained from (3.21) or be written as

$$H_D(q=0)=2^D I_{1-1/a^2}((D+1)/2,1/2)$$
$$-\tfrac{1}{2}a^D I_{1-(1-2/a^2)^2}((D+1)/2,1/2) \quad (3.23)$$

and evaluated in practice from the recurrence relation (A10). For instance,

$$H_1(q=0;a)=2-a-\frac{1}{a}, \quad (3.24)$$

$$H_2(q=0;a)=\frac{2}{\pi}(4-a^2)\arccos\frac{1}{a} - \frac{2}{\pi}\left[a+\frac{2}{a}\right]\left[1-\frac{1}{a^2}\right]^{1/2}, \quad (3.25)$$

$$H_3(q=0;a)=8-\frac{9}{a}+\frac{2}{a^3}-a^3, \quad (3.26)$$

$$H_4(q=0;a)=\frac{2}{\pi}(16-a^4)\arccos\frac{1}{a} - \frac{2}{\pi}\left[\frac{2a}{3}+\frac{56}{3a}-\frac{16}{3a^2}+a^3\right]\left[1-\frac{1}{a^2}\right]^{1/2}, \quad (3.27)$$

$$H_5(q=0;a)=32-\frac{50}{a}+\frac{25}{a^3}-\frac{6}{a^5}-a^5. \quad (3.28)$$

It then results from (3.22) that provided B_2 and B_3 are exact for the given $Z(\eta)$, $a(\eta=0)=2$, as implied by the low-density result (3.5), and provided $\{\partial/\partial\eta[\eta Z(\eta)]\}^{-1}$ vanishes as $\eta\rightarrow 1$ for the given $Z(\eta)$, $a(\eta=1)=1$, whereas in between $(0<\eta<1)$ $a(\eta)$ decreases monotonically from 2 to 1 as η increases from 0 to 1.

Our ansatz provides thus an explicit expression for $c(x;\eta)$ and up to the one-dimensional integral (3.21) also for $S(q;\eta)$. To test the results we now consider some explicit examples.

A. Hard rods ($D=1$)

In this particular case (3.22) degenerates into a trivial identity satisfied by any $a(\eta)$ when $Z(\eta)=(1-\eta)^{-1}$ [see (2.20)]. This is due to the fact that for $D=1$ the DCF of (3.10) is scale invariant [viz, $1-a\eta+a\eta(1-x/a)\equiv 1-\eta x$]. We thus obtain for (3.10) and (3.19) using (2.20)

$$c(x;\eta)=-\Theta(1-x)\frac{(1-x\eta)}{(1-\eta)^2}, \quad (3.29)$$

$$c(q;\eta)=-\frac{\eta}{(1-\eta)^2}\{(1-\eta)2f_{1/2}(q)+\eta[f_{1/2}(q/2)]^2\}, \quad (3.30)$$

with $f_{1/2}(q)=q^{-1}\sin q$ [see (3.20)]. We thus recover the exact results for $D=1$.

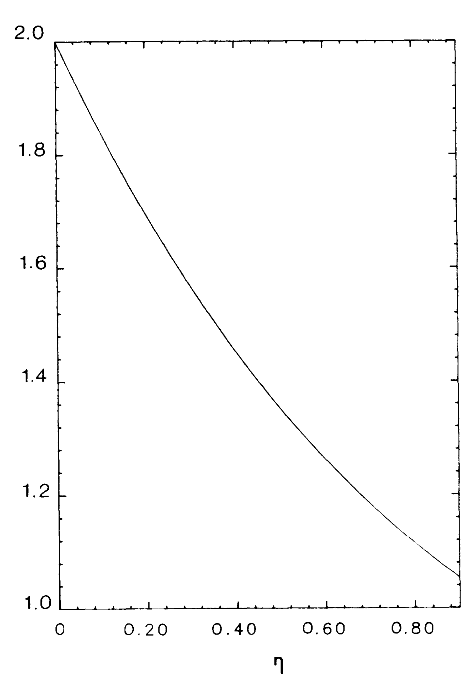

FIG. 6. The solution $a=a(\eta)$, of Eq. (3.32) ($D=2$) for $Z=Z_6(\eta)$ of Eq. (2.18).

B. Hard disks ($D=2$)

This case is of particular interest since no analytic results (exact or approximate) are known for the structure of hard-disk fluids. From (3.10)–(3.12) we obtain

$$c(x;\eta)=-\frac{\partial}{\partial\eta}[\eta Z(\eta)]\Theta(1-x)\left\{1-a^2\eta+\frac{2}{\pi}a^2\eta\left[\arccos\frac{x}{a}-\frac{x}{a}\left[1-\frac{x^2}{a^2}\right]^{1/2}\right]\right\}, \quad (3.31)$$

where $a=a(\eta)$ is obtained from (3.22–3.25) by solving the equation

$$\frac{2}{\pi}\left[a^2(a^2-4)\arcsin\left[\frac{1}{a}\right]-(a^2+2)(a^2-1)^{1/2}\right] = \frac{1}{\eta^2}\left[1-4\eta-\left[\frac{\partial}{\partial\eta}[\eta Z(\eta)]\right]^{-1}\right], \quad (3.32)$$

with $Z(\eta)$ taken from Sec. II. The structure factor is then obtained from (3.19) but here (3.21) has to be evaluated numerically.

The result, $a=a(\eta)$ of (3.32) for $Z=Z_6(\eta)$ of (2.18) is shown in Fig. 6. A simple numerical fit to the solution curve of (3.32) for $Z=Z_2(\eta)$ was given elsewhere.[3] In general $a(\eta)$ shows little sensitivity to $Z(\eta)$ because for small η values $a(\eta)$ is exact while for large η the

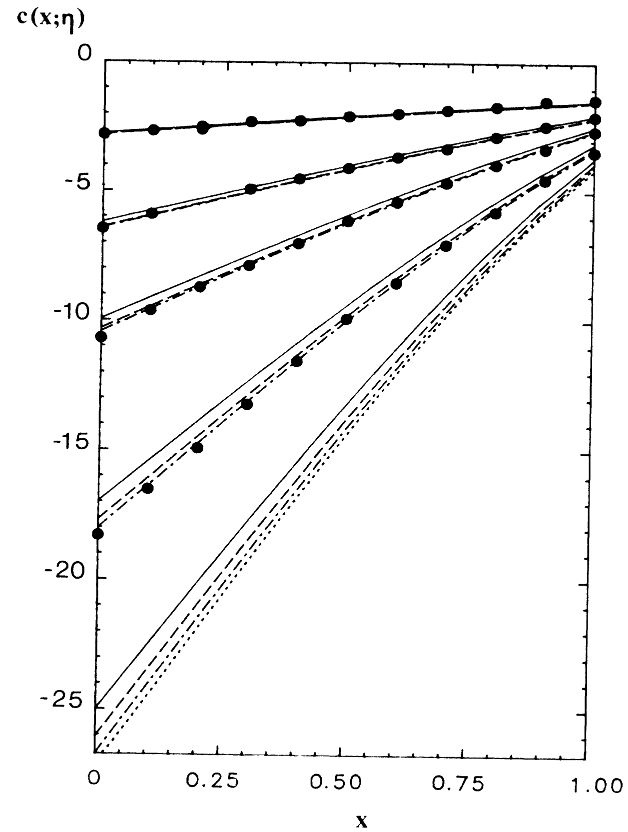

FIG. 7. The DCF $c(x;\eta)$ for hard disks ($D=2$) as obtained from (3.31) and (3.32) for $Z=Z_0$ (——), Z_2, (—·—·—·), and Z_6 (— — —) of (2.18) compared to the numerical solution of the PY equations as obtained by Lado (Ref. 18) for (from top to bottom) $\rho\sigma^2=0.3,0.5,0.6,0.7$ (large dots) and $\eta=0.6$ (small dots) [Lado (private communication)].

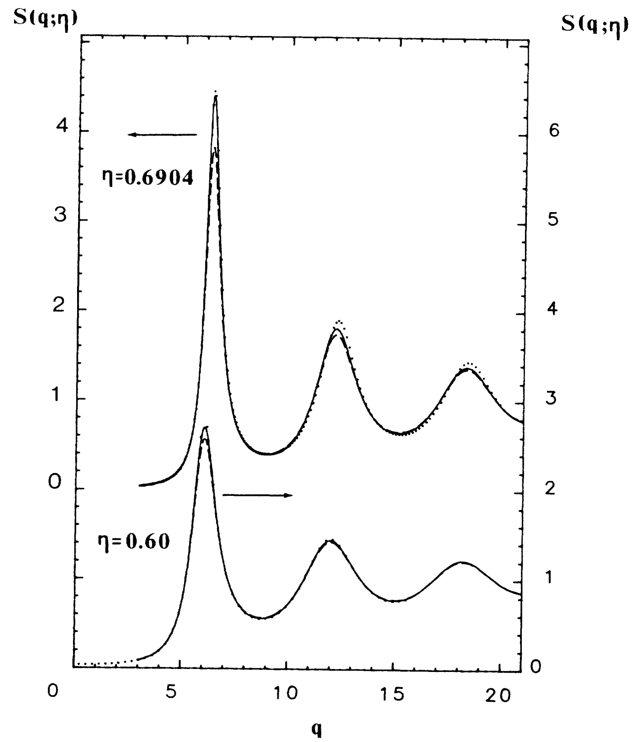

FIG. 8. The static structure factor $S(q;\eta)$ for hard disks ($D=2$) as obtained from (3.19) and (3.32) for $Z=Z_2$ (——) and Z_6 (— — —) of (2.18) compared to the result of the numerical solution of (a) the PY equation at $\eta=0.60$ (· · · ·) [Lado (private communication)] and (b) the integral equation of Verlet and Levesque (Ref. 19) at $\eta=0.6904$ (· · · ·) [J. J. Weis (private communication)].

compressibility entering Eq. (3.22) is small. As a result, $c(x;\eta)/c(x=0;\eta)$, also shows little sensitivity to $Z(\eta)$ so that the major source of errors stems from the isothermal compressibility generated by $Z(\eta)$ which determines the overall scale $c(x=0;\eta)$ via Eq. (3.8). In Fig. 7 we compare to the DCF $c(x;\eta)$ as obtained from (3.31) and (3.32) for $Z=Z_0$, Z_2, and Z_6 of (2.18) to the results obtained by Lado[18] from the numerical solution of the PY equation. The differences in the corresponding isothermal compressibilities are visible in Fig. 7 at $x=0$. In Fig. 8 we compare the structure factor obtained from (3.19) for $Z=Z_2$ and Z_6 of (2.18) to the results of the numerical solution of the PY equations[18] and of the integral equation proposed by Verlet and Levesque.[19] The changes in the height of the main peak of $S(q;\eta)$ are again monitored by the isothermal compressibility of the underlying equation of state.

C. Hard spheres ($D=3$)

Fairly accurate data for the hard spheres have been obtained in the literature from the PY approximation and the modifications thereof. This case serves thus as a testing ground for our general proposal. Equation (3.10) now reduces to

$$c(x;\eta)=-\frac{\partial}{\partial\eta}[\eta Z(\eta)]\Theta(1-x)(1-\tfrac{3}{2}\eta a^2 x+\tfrac{1}{2}\eta x^3)\ , \tag{3.33}$$

whereas (3.22) yields

$$a^2=\frac{1}{9\eta^2}\left[2\eta^2+8\eta-1+\left[\frac{\partial}{\partial\eta}[\eta Z(\eta)]\right]^{-1}\right] \tag{3.34}$$

or combining (3.34) and (3.33)

$$c(x;\eta)=-\frac{\partial}{\partial\eta}[\eta Z(\eta)]\Theta(1-x)\left\{1+\frac{1}{2}\eta x^3-\frac{x}{6\eta}\left[2\eta^2+8\eta-1+\left[\frac{\partial}{\partial\eta}[\eta Z(\eta)]\right]^{-1}\right]\right\}. \tag{3.35}$$

For the structure factor we obtain for (3.19), integrating (3.21) explicitly

$$c(q;\eta)=-\eta\frac{\partial}{\partial\eta}[\eta Z(\eta)]\left[\frac{12}{q^6}(24\eta+6\eta a^2q^2)+\frac{12}{q^6}\cos(q)[-24\eta+q^2(12\eta-6\eta a^2)-q^4(2+\eta-3\eta a^2)]\right.$$
$$\left.+\frac{12}{q^5}\sin(q)[-24\eta+q^2(2+4\eta-6\eta a^2)]\right], \quad (3.36)$$

where (3.34) defines $a=a(\eta)$.

Using for $Z(\eta)$ the value $Z_{\text{PY-}c}(\eta)$ [see (2.22) with $a=0=b$] reduces Eqs. (3.35) and (3.36) to the well-known PY results.[1] In Fig. 9 we compare the structure factor obtained from (3.36) with $Z=Z_4(\eta)$ of (2.18) to the result of the PY theory [identical to our result for $Z=Z_2(\eta)$] and to the proposal of Verlet and Weis.[25]

D. Hard hyperspheres ($D>3$)

The only result for the structure known to us when $D>3$ is the analytic solution of the PY equations for $D=5$ obtained by Freasier and Isbister[12] and also by Leutheusser,[23]

$$\begin{aligned}&c(x;\eta)=\Theta(1-x)(c_0+c_1x+c_3x^3+c_5x^5)\,,\\&c_0=-(8Q_2)^2\,,\\&c_1=120\eta(Q_0)^2\,,\\&c_3=20\eta(8Q_0Q_2-3Q_1^2)\,,\\&c_5=-\tfrac{3}{8}\eta c_0=24\eta(Q_2)^2\,,\end{aligned}\quad (3.37)$$

where Q_0 and Q_2 have been introduced above [see (2.25) and (2.26)] and Q_1 is given by

$$Q_1=\frac{-1}{12(1-\eta)^3}[(3+2\eta)(1+18\eta+6\eta^2)^{1/2}+3+19\eta+3\eta^2]\,. \quad (3.38)$$

For the sake of comparison we also quote the corresponding $D=5$ result from (3.10) and (3.22),

$$c(x;\eta)=-\frac{\partial}{\partial\eta}[\eta Z(\eta)]\Theta(1-x)\times(1-\tfrac{15}{8}a^4\eta x+\tfrac{5}{4}a^2\eta x^3-\tfrac{3}{8}\eta x^5)\,, \quad (3.39)$$

$$a^2=\frac{1}{4}+\frac{1}{120\eta}\left[256\eta-23\eta^2-8+8\left[\frac{\partial}{\partial\eta}[\eta Z(\eta)]\right]^{-1}\right]^{1/2}. \quad (3.40)$$

In Figs. 10 and 11 we compare the DCF and the structure factor of the PY theory to those corresponding to (3.39) and (3.40).

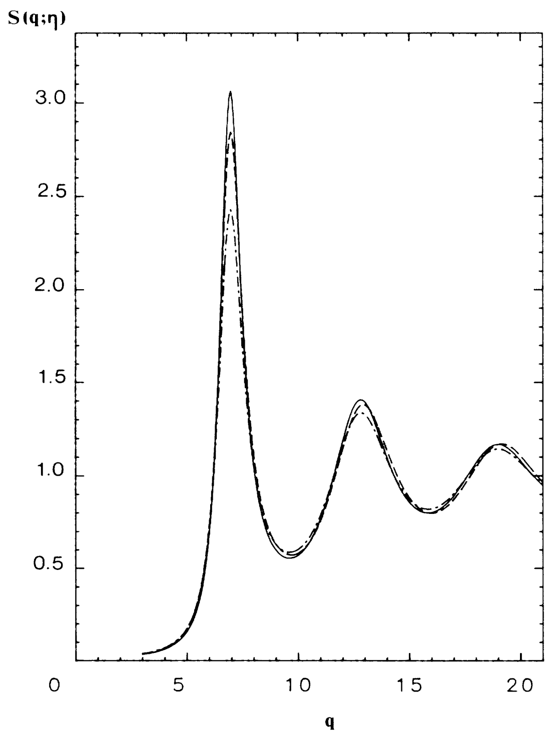

FIG. 9. The static structure factor $S(q;\eta)$ for hard spheres ($D=3$) at $\eta=0.49$ as obtained from (3.36) for Z_2 (——) and $Z=Z_4$ (—·—·—·) of (2.18) compared to the results of Verlet and Weis (Ref. 25) (— — —).

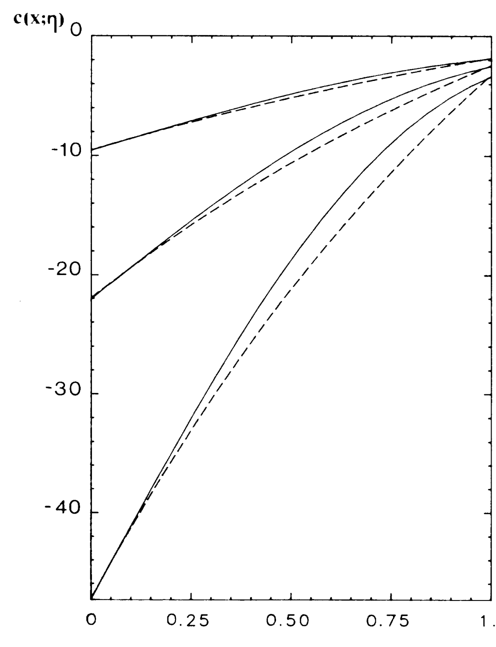

FIG. 10. The DCF $c(x;\eta)$ for hard hyperspheres ($D=5$) as obtained from (3.39) for $Z=Z_2$ (——) of (2.18) compared to the result of the PY theory (— — —) of (3.37) for (from top to bottom) $\eta=0.10$, 0.15, and 0.20.

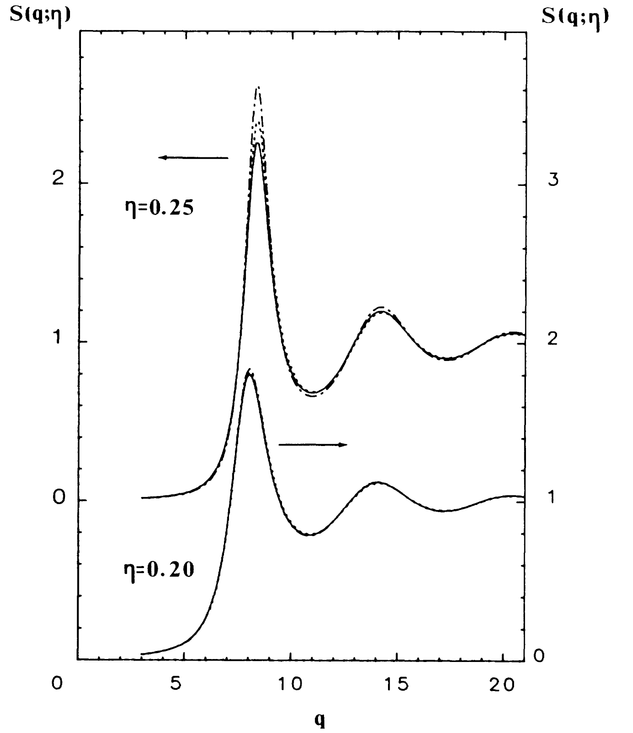

FIG. 11. The static structure factor $S(q;\eta)$ for hard hyperspheres ($D=5$) as obtained from (3.39) and (3.40) for $Z=Z_2$ (——) and Z_4 (—·—·—·) of (2.18) compared to the result of the PY theory (· · · ·) as obtained from (3.37) for $\eta=0.20$ and 0.25.

IV. CONCLUSIONS

We have considered the practical problem of constructing simple and accurate expressions for the thermodynamic and structural properties of a fluid of hard D-spheres whatever the value of D, odd or even. Our proposal is based on a simple rescaling of the low-density expressions of the equation of state [see (2.11)] and of the direct correlation function [see (3.7)]. These rescaled expressions, while remaining exact at low density, yield fairly accurate data also at the higher densities for all space dimensionalities D where comparison with computer simulation results is possible ($1 \leq D \leq 5$). For $D=1$ the results are exact whereas for $D=3$ well-known results, such as the Percus-Yevick theory, are easily recovered. Excellent results have also been obtained for the important case of hard disks ($D=2$). There is no difficulty in extending our results to higher D values or to noninteger values of D. A first application has already been presented elsewhere.[4] We observe that the overall form of the structure factor is very well reproduced by our simple expressions whereas the well-known difficulties with the height of the main peak of the structure factor have been tracked back to inaccuracies in the underlying isothermal compressibility. The main drawback of our method is that the determination of the structure requires the thermodynamics as input. Alternative procedures are possible[24] but quickly become impractical.

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APPENDIX A: THE THIRD VIRIAL COEFFICIENT

In D-space we have for any function $f(\mathbf{x})$ depending only on the distance $x=|\mathbf{x}|$,

$$\int d\mathbf{x}\, f(x)=S_D \int_0^\infty dx\, x^{D-1} f(x) \,, \tag{A1}$$

or on x and one integration angle θ,

$$\int d\mathbf{x}\, f(x,\theta)=S_{D-1} \int_0^\infty dx\, x^{D-1} \int_0^\pi d\theta \sin^{D-2}\theta f(x,\theta) \,, \tag{A2}$$

where $S_D = DV_D$ is the surface area of the unit sphere of volume $V_D=\pi^{D/2}/\Gamma(1+D/2)$. The Fourier transform of the Heaviside unit step function $\theta(1-x)$ becomes then in reduced variables ($\mathbf{x}=\mathbf{r}/\sigma;\mathbf{q}=\mathbf{k}\sigma$)

$$\int d\mathbf{x}\, e^{i\mathbf{q}\cdot\mathbf{x}}\theta(1-x)=\left[\frac{2\pi}{q}\right]^{D/2} J_{D/2}(q) \equiv V_D f_{D/2}(q) \,, \tag{A3}$$

where $J_D(q)$ is the Bessel function related to $f_D(q)$ by (3.20). The third virial coefficient B_3

$$B_3=\tfrac{1}{3}\int d\mathbf{r} \int d\mathbf{r}'\, \theta(\sigma-|\mathbf{r}|)\theta(\sigma-|\mathbf{r}'|)\theta(\sigma-|\mathbf{r}-\mathbf{r}'|) \tag{A4}$$

can then be written using the Fourier inverse of (A3),

$$B_3=\frac{D 2^{D/2}\pi^D\sigma^{2D}}{3\Gamma(1+D/2)} \int_0^\infty dq\, q^{-1-D/2}[J_{D/2}(q)]^3 \,, \tag{A5}$$

which is a nonstandard integral not included in the recent survey by Gervois and Navelet.[26] To compute (A5) we use Eq. (6.683.7) of Gradshteyn and Ryzhik[27] to eliminate a Bessel function squared in favor of an integral over a single Bessel function. The resulting product of two different Bessel functions remaining in (A5) can then be integrated by using Eq. (6.576.2) of Grad shteyn and Ryzhik.[27] There results a hypergeometric function which can be simplified further on using Eq. (15.1.13) of Abramowitz and Stegun.[28] The final result is given then by (2.6) in terms of the normalized incomplete beta function,[28]

$$I_x(a,b)=\frac{B_x(a,b)}{B(a,b)} \,, \tag{A6}$$

defined in terms of the beta function[28] $B(a,b)$

$$B(a,b)=\Gamma(a)\Gamma(b)/\Gamma(a+b) \tag{A7}$$

and the incomplete beta function[28] $B_x(a,b)$

$$B_x(a,b)=\int_0^x dt\, t^{a-1}(1-t)^{b-1}\ , \tag{A8}$$

with $B_1(a,b)\equiv B(a,b)$ and $I_1(a,b)=1$. Some useful properties[28] are

$$I_x(a,b)=1-I_{1-x}(b,a)\ , \tag{A9}$$

$$I_x(a,b)=I_x(a+1,b)+\frac{\Gamma(a+b)}{\Gamma(a+1)\Gamma(b)}x^a(1-x)^b\ , \tag{A10}$$

and the particular cases

$$I_x((D+1)/2,\tfrac{1}{2})=\frac{2}{B((D+1)/2,\frac{1}{2})}\times\int_0^{\arccos\sqrt{1-x}} d\theta(\sin\theta)^D\ , \tag{A11}$$

$$I_x(\tfrac{1}{2},\tfrac{1}{2})=\frac{2}{\pi}\arccos\sqrt{1-x}\ , \tag{A12}$$

$$I_x(1,\tfrac{1}{2})=1-\sqrt{1-x}\ , \tag{A13}$$

which will be frequently encountered in the main text.

APPENDIX B: THE OVERLAP VOLUME

The normalized overlap volume of (3.6), $\omega_D(x)$, can be written using (A3) and the general result

$$\int d\mathbf{q}\, e^{i\mathbf{q}\cdot\mathbf{x}}f(q)=\frac{(2\pi)^{D/2}}{x^{(D-2)/2}}\int_0^\infty dq\, q^{D/2}J_{D/2-1}(qx)f(q) \tag{B1}$$

as

$$\omega_D(x)=\frac{2^{D/2}}{x^{(D-2)/2}}\Gamma(1+D/2)\int_0^\infty dq\, q^{-D/2}J_{D/2-1}(qx)\times[J_{D/2}(q/2)]^2\ , \tag{B2}$$

which is also a nonstandard integral.[26] To compute (B2) we again eliminate the square of the Bessel function with the aid of Eq. (6.683.7) of Gradshteyn and Ryzhik.[27] The result is now a standard integral over a product of two Bessel functions[27] which finally leads to the result quoted in (3.11).

APPENDIX C: THE STRUCTURE FACTOR

Frome (3.10) we obtain using (A3), (B1), and (3.20)

$$c(q;\eta)=-\eta\frac{\partial}{\partial\eta}[\eta Z(\eta)][(1-a^D\eta)2^Df_{D/2}(q)+a^D\eta F_D(q;a)]\ , \tag{C1}$$

where

$$F_D(q;a)=\frac{[2^D\Gamma(1+D/2)]^2}{q^{(D-2)/2}}\times\int_0^1 dx\, x\int_0^\infty dy\, y^{-D/2}J_{D/2-1}(qx)\times J_{D/2-1}(yx)[J_{D/2}(ay/2)]^2 \tag{C2}$$

is again simplified by eliminating the squared Bessel function as above. The resulting y integral is a standard integral[27] over a product of two Bessel functions. Evaluating also the remaining x integral over a single Bessel function[27] we obtain for (C2)

$$F_D(q;a)=\frac{[2^D\Gamma(1+D/2)]^2}{2^{(D-2)/2}\sqrt{\pi}\Gamma((D+1)/2)}\left[\frac{a}{q}\right]^{D/2}\left[\int_0^{\theta_0} d\theta(\cos\theta)^D(\sin\theta)^{D/2}J_{D/2}(aq\sin\theta)+\int_{\theta_0}^{\pi/2} d\theta(\cos\theta)^D(\sin\theta_0)^{D/2}J_{D/2}(aq\sin\theta_0)\right]\ , \tag{C3}$$

with $\theta_0=\arcsin(1/a)$. Equation (C3) is then further transformed into

$$F_D(q;a)=[a^{D/2}f_{D/2}(aq/2)]^2+H_D(q;a)\ , \tag{C4}$$

where the definitions (3.20) and (3.21) have been used. Substituting (C4) into (C1) leads then to the result quoted in (3.19). The integral remaining in (3.21) can be evaluated analytically only for the odd D values.

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