UvA-DARE (Digital Academic Repository)

Equation of State of Hard D-Dimensional Hyperspheres

Luban, M.; Michels, J.P.J.

DOI

[10.1103/PhysRevA.41.6796](https://doi.org/10.1103/PhysRevA.41.6796)

Publication date

1990

Published in

Physical Review A

[Link to publication](#)

Citation for published version (APA):

Luban, M., & Michels, J. P. J. (1990). Equation of State of Hard D-Dimensional Hyperspheres. *Physical Review A*, 41, 6796-6804. <https://doi.org/10.1103/PhysRevA.41.6796>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Equation of state of hard D -dimensional hyperspheres

Marshall Luban

Ames Laboratory and Department of Physics, Iowa State University, Ames, Iowa 50011

J. P. J. Michels

van der Waals Laboratory, University of Amsterdam, Amsterdam, The Netherlands

(Received 11 January 1990)

We present an expression providing an accurate representation, for all densities, of Monte Carlo-molecular-dynamics (MCMD) equation-of-state data for the fluid phase of hard D -dimensional hyperspheres (D -spheres), with $D=2-5$. This expression incorporates the exact values of the virial coefficients B_2 , B_3 , B_4 , and two constants determined from the MCMD data.

I. INTRODUCTION

Computer simulations using Monte Carlo and molecular-dynamics (MCMD) methods are providing precision empirical data for the equation of state (EOS) of systems of hard D -dimensional hyperspheres (D -spheres), i.e., disks,¹ spheres,² and hyperspheres³ with dimensionality $D=4,5$. Perhaps the most interesting aspect of these systems is their great similarity. For example, each of these systems⁴ has been found to exhibit a first-order freezing transition. For increasing values of D the density of this transition, measured in units of the density of closest lattice packing, decreases monotonically. The only equilibrium quantities that have been calculated to date for the systems with $D=4,5$ are the values of the three virial coefficients^{5,6} B_2 , B_3 , B_4 . One therefore expects that, with the exception of the low-density regime, it would be difficult if not impossible to construct an accurate representation of the EOS of these systems based on just these three virial coefficients.

In this article we explore the question of what minimal information, supplementary to the virial coefficients B_2 , B_3 , B_4 , might provide an accurate representation of the MCMD data for the fluid phase, for all densities extending to the freezing transition, of systems of hard D -spheres for $D=2-5$. As a first step we express the EOS as a ratio of two functions [see Eqs. (2)–(4)], where each depends upon the particle number density ρ and incorporates the three virial coefficients B_2 , B_3 , and B_4 as well as an arbitrary function of ρ , $\zeta(\rho)$, to be determined using the existing MCMD data. The primary result of the present work is our finding that a *linear* approximation for $\zeta(\rho)$ leads to a very good representation of the best available MCMD data for hard D -spheres for all densities extending to the freezing transition.

In this work we provide a common treatment for all dimensionalities, and in particular, we specifically refrain from using higher-order virial coefficients, even though several accurate values are known⁷ for the hard-disk and hard-sphere systems. (In fact, for the latter two systems the EOS's given in Refs. 1 and 2 provide an extremely accurate representation of the best available MCMD data.) The reason for our approach, of refraining from utilizing

higher-order virial coefficients in the case of the hard-disk and hard-sphere systems, is the following. The absence of higher-order virial coefficients for hard 4- and 5-spheres is characteristic of the situation for realistic two-body interatomic and intermolecular potentials. Specifically, for these realistic systems it is feasible to obtain accurate values of B_2 , B_3 , and B_4 , whereas the calculation of B_5 and higher-order virial coefficients is extremely difficult. The success of the present approach for hard D -spheres warrants exploring whether an expression of the form (2)–(4), requiring knowledge of B_2 , B_3 , and B_4 together with a simple choice for ζ , a function of both ρ and T , might yield an accurate EOS for real fluids over a wide range of densities and temperatures. We are actively pursuing this question at the present time.

The details for each specific dimensionality ($D=2-5$) are provided in Secs. III–VI. Finally, in Sec. VII we summarize our present results.

II. BEYOND THE VIRIAL EXPANSION

After reviewing the limitations of representing the EOS for the fluid phase of hard D -sphere systems by the virial expansion, we present a preferable form, given by Eqs. (2)–(4).

The standard virial expansion of the EOS for the fluid phase of hard D -spheres can be written as

$$\Xi(x) = p/(\rho k_B T) - 1 = \sum_{n=2}^{\infty} B_n^* x^{n-1}, \quad (1)$$

where p is the pressure, ρ is the number density, k_B is Boltzmann's constant, T is the absolute temperature, the B_n^* are given in terms of the virial coefficients B_n by $B_n^* = B_n \rho_c^{n-1}$, $x = \rho/\rho_c$, and ρ_c is the number density associated with closest-lattice packing. The exact values of the virial coefficients B_2, B_3, B_4 , for the hard-disk and hard-sphere systems have been known for decades. Numerical estimates of B_5, B_6, B_7 are also available⁷ for these systems. Only in recent years has there been interest in the corresponding quantities for hard D -spheres of arbitrary dimensionality. The exact values of the quantities B_2, B_3 as well as two of the three terms which contribute to B_4 were first derived in Ref. 5 for arbitrary values of

TABLE I. Values of number density ρ_c for closest-lattice packing and the known virial coefficients for hard D -spheres of diameter a and dimensionality D .

D	2	3	4	5
$\rho_c a^D$	$\frac{2}{\sqrt{3}}$	$\sqrt{2}$	2	$2\sqrt{2}$
B_2/a^D	$\frac{\pi}{2}$	$\frac{2\pi}{3}$	$\frac{\pi^2}{4}$	$\frac{4\pi^2}{15}$
$B_3/(B_2)^2$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}$	$\frac{5}{8}$	$\frac{4}{3} - \frac{3\sqrt{3}}{2\pi}$	$\frac{53}{128}$
$B_4/(B_2)^3$	0.532 231 807 025	0.286 949 505 982	0.151 846 054 (20) ^a	0.075 972 512(4) ^a
$B_5/(B_2)^4$	0.333 556 04(4) ^b	0.110 252(1) ^b		
$B_6/(B_2)^5$	0.198 83(1) ^b	0.0389(4) ^b		
$B_7/(B_2)^6$	0.1148(5) ^b	0.0137(6) ^b		

^a Source, from Ref. 5 (Table I) and Ref. 6.

^b Source, from Ref. 7.

D . Recently⁶ the remaining unknown contribution to B_4 , $B_4(\boxtimes)$ in the notation of Ref. 5, has been evaluated by analytical methods for $D=4,5$. At the present time there are no estimates, as obtained by direct calculation, of B_5 or higher-order virial coefficients for the cases $D=4,5$. All available exact and estimated values of the virial coefficients for $D=2-5$ are listed in Table I.

In view of the paucity⁸ of known virial coefficients, the obvious shortcoming of the power series expansion (1) is that it is useful only for the regime of very low densities. A far more useful representation of Ξ , one which can be employed for arbitrary densities, consists of expressing Ξ as

$$\Xi(x) = S(x; \zeta) / T(x; \zeta), \quad (2)$$

where

$$S(x; \zeta) = B_2^* x \{ 1 + [(B_3^* / B_2^*) - \zeta(x)(B_4^* / B_3^*)]x \}, \quad (3)$$

$$T(x; \zeta) = 1 - \zeta(x)(B_4^* / B_3^*)x + [\zeta(x) - 1](B_4^* / B_2^*)x^2. \quad (4)$$

The sole restriction imposed on the function $\zeta(x)$ is that it is analytic in the vicinity of the origin of the complex x plane and thus it admits a convergent⁹ Taylor series in powers of x . Hence the representation (2)–(4) does not entail any approximation whatsoever. Note that even if

one adopts the choice $\zeta(x) \equiv 0$, the ratio $S(x; 0) / T(x; 0)$ provides an EOS in the form of a rational approximant, a representation which is decidedly superior to that of a polynomial truncation of the power series (1). More generally, whatever the choice of $\zeta(x)$, the specific forms chosen for $S(x; \zeta)$ and $T(x; \zeta)$ ensure that if (2) is expanded in powers of x , one obtains $\Xi(x) = B_2^* x + B_3^* x^2 + B_4^* x^3 + C_5 x^4 + \dots$. That is, the first three terms of this expansion are independent of the form of $\zeta(x)$. The Taylor coefficients of ζ manifest themselves only in the coefficients C_n , $n \geq 5$. If $\zeta(x)$ is provided, the C_n can be viewed as giving estimates for the values of the coefficients B_n^* for $n \geq 5$. Alternately, if $\Xi(x)$ is given, inverting (2)–(4) yields the following explicit expression for ζ :

$$\zeta(x) = \frac{B_3^* [B_2^* x (B_2^* + B_3^* x) - (B_2^* - B_4^* x^2) \Xi(x)]}{B_4^* x [(B_2^*)^2 x + (B_3^* x - B_2^*) \Xi(x)]}. \quad (5)$$

The lone factor x in the denominator of (5) would appear to give rise to a simple pole of ζ at $x=0$ contradicting our requirement that it be analytic in the vicinity of the origin. However, upon using (1), this factor is canceled. In fact, one can generate the complete Taylor series expansion of $\zeta(x)$ in terms of the full set of scaled virial coefficients B_n^* . For later use we remark that

$$\zeta(0) = (B_3^* / B_4^*) (B_3^* B_4^* - B_2^* B_5^*) / (B_3^{*2} - B_2^* B_4^*). \quad (6)$$

TABLE II. Values of Ξ for a system of hard disks: MCMD data of Ref. 1; Eqs. (2)–(4) with $\zeta(x) = 1.5317 - 0.0627x$; the Levin T approximant given in Ref. 1; the [3/2] and [2/3] Padé approximants to the virial series given in Ref. 1. As discussed in the text, the entries with an asterisk have been set equal to the corresponding Levin T estimates.

$x = \rho / \rho_c$	MCMD	Present method	Levin T	Padé[3/2]	Padé[2/3]
0.1000	0.210 68(3)	0.210 69*	0.210 69	0.210 69	0.210 69
0.2000	0.4983(1)	0.498 43*	0.498 43	0.498 43	0.498 43
0.3333	1.0771(2)	1.077 20*	1.077 20	1.077 15	1.077 26
0.5000	2.4243(3)	2.4243	2.424 03(7)	2.422 68(7)	2.4261(1)
0.5556	3.1715(4)	3.1712	3.1707(2)	3.1670(2)	3.1767(3)
0.6250	4.4963(6)	4.4956	4.4948(5)	4.4818(5)	4.516(1)
0.6667	5.6074(6)	5.6092	5.6087(9)	5.5812(9)	5.655(2)
0.7143	7.306(1)	7.343*	7.343(2)	7.278(2)	7.456(4)

The practical usefulness of (2)–(4) stems from our finding that, upon using the existing MCMD data for each of $D=2-5$, a linear form, namely $\zeta(x)=\zeta_L(x)\equiv\zeta_0+\zeta_1x$, provides a very accurate representation of Ξ for the fluid phase for all densities up to the fluid-solid transition. In the following, $\Xi_L(x)$ will denote the form of the function Ξ when $\zeta(x)$ is approximated by $\zeta_L(x)$. That is, $\Xi_L(x)\equiv S(x;\zeta_L)/T(x;\zeta_L)$.

In the remaining sections of this work we will have occasion to use the following formulas for the Taylor coefficients when Ξ_L is expanded in powers of x ,

$$\Xi_L(x)=S(x;\zeta_L)/T(x;\zeta_L)=\sum_n \hat{C}_{n+1}x^n. \quad (7)$$

These Taylor coefficients are denoted by $\hat{C}_n$ to underscore the fact that they differ in general from the expansion coefficients C_n of Ξ for an arbitrary (nonlinear) choice of $\zeta(x)$. The infinite sum in (7) starts with $n=1$, and the Taylor coefficients are given by $\hat{C}_2=B_2^*$, $\hat{C}_3=B_3^*$, $\hat{C}_4=B_4^*$, as well as

$$\begin{aligned} \hat{C}_n/B_4^* &= (\hat{C}_{n-1}\zeta_0 + \hat{C}_{n-2}\zeta_1)(1/B_3^*) \\ &+ [\hat{C}_{n-2}(1-\zeta_0) - \hat{C}_{n-3}\zeta_1](1/B_2^*) \end{aligned} \quad (8)$$

for $n \geq 5$.

We now proceed to use MCMD fluid phase data to demonstrate the approximate linearity of $\zeta(x)$ for hard D -spheres. We first treat the case $D=2$ and then proceed to consider larger values of D .

III. HARD DISKS

The best available EOS data for the hard-disk system, estimated to have an accuracy of 1 part in 10^4 , are listed in the second column of Table II. They were obtained¹ by MCMD methods for systems of up to 5822 particles. This system undergoes a first-order freezing transition¹⁰ for $\rho \approx 0.76\rho_c$. It was also shown in Ref. 1 that a Levin T approximant, applied to the first five terms of the series (1) and free of any adjustable parameters, provides values of Ξ which are in excellent agreement with the MCMD data. These data appear in the fourth column of Table II. We believe, then, that the Levin T approximant provides a highly satisfactory first-principles theory of the fluid phase of the hard-disk system. We also list in the fifth and sixth columns of Table II the values of the pair of Padé approximants $[3/2],[2/3]$ constructed using B_2-B_6 . The listed uncertainties¹ for the Levin and Padé approximants stem from the uncertainty in the value of B_6 .

In keeping with the purpose of this article, in the following we utilize only B_2 , B_3 , and B_4 along with the EOS data for Ξ and (5) to generate values of $\zeta(x)$. As remarked in Sec. II the values of $\zeta(x)$ are determined by the discrepancy between the actual EOS and the sum of the first three terms of the virial series (1). Therefore, in the low-density regime, even very small numerical uncertainties in the MCMD data for Ξ are greatly magnified in the course of using (5). To circumvent this difficulty, for $x=0.1, 0.2$, and 0.3333 , rather than employ the MCMD data, we adopt the Levin T estimates for Ξ . We view the

agreement between the Levin and Padé estimates for these three values of x as justifying these choices. Furthermore, for the purpose of determining the value of ζ at the highest density $x=0.7143$, we arbitrarily set Ξ equal to the Levin estimate 7.343. The resulting eight values of ζ are shown in Fig. 1. The data suggest that the function $\zeta(x)$ is very well approximated by a linear function of x . A linear least-squares analysis, whereby the same¹¹ uncertainty is adopted for all values of ζ , yields $\zeta_L(x)=\zeta_0+\zeta_1x$, with $\zeta_0=1.5317(3)$ and $\zeta_1=-0.0627(6)$. Although the form of $\zeta_L(x)$ is derived using values of Ξ for the restricted interval (0.1,0.7143) it is remarkable that the extrapolated value of $\zeta_L(0)$, given by $\zeta_0=1.5317$, agrees with $\zeta(0)$ of Eq. (6) at the level of better than 2 parts in 10^4 . Specifically, if we substitute in (6) the values of the virial coefficients given in Table I for the hard-disk system, one obtains $\zeta(0)=1.53141$.

In the third column of Table II we list the values of Ξ as given by the representation (2)–(4) along with the choice $\zeta\equiv\zeta_L(x)=1.5317-0.0627x$. It will be noted that these results cannot be distinguished at the 1.0-standard-deviation level from those generated by the Levin T approximant. Note that the Levin T approximant takes the form¹ of a ratio of two polynomials, each of degree 5. By contrast, Ξ_L takes the form of a ratio of two polynomials each of degree 3. On the other hand, the Levin T approximant is free of any adjustable parameters, being determined solely in terms of the virial coefficients B_2-B_6 .

The quantity $\hat{C}_n/(B_2\rho_c)^{n-1}$ provides an estimate for $B_n/(B_2)^{n-1}$. Using (8) along with the above values of ζ_0 and ζ_1 we find that for $n=5-7$ the corresponding estimates for $B_n/(B_2)^{n-1}$ are 0.333 538, 0.198 95, and 0.114 96, respectively. The first of these three values agrees with the best current estimate of $B_5/(B_2)^4$ at the

FIG. 1. Data (+) for ζ vs reduced density x for a system of hard disks upon using Eq. (5) and values (Ref. 1) of the virial Ξ obtained by MCMD and Levin approximant methods, as specified in the text. A linear least-squares analysis of this data yields $\zeta(x)=1.5317-0.0627x$, shown as the solid line. The lone point shown as (Δ) is the value of ζ for $x=0.7143$ as obtained employing the MCMD value of Ξ for a system of 5822 hard disks.

level of 5 parts in 10^5 .

We have also obtained an estimate for ζ_1 upon requiring that $\zeta_L(0)$ agree with the value of $\zeta(0)$. If $\zeta(x)$ were strictly linear in x the ratio $[\zeta(x) - \zeta(0)]/x$ would be independent of x and equal to ζ_1 . Indeed, we find that $[\zeta(x) - \zeta(0)]/x$ is very nearly constant, given by $-0.0617(3)$, when we use our eight numerical values of ζ . This result is in good agreement with the estimate of ζ_1 given above, obtained without imposing a constraint on ζ_0 .

If we adopt the MCMD value for Ξ at $x=0.7143$, the resulting value for ζ derived from (5), denoted by the symbol Δ in Fig. 1, departs sharply from the linear pattern which occurs for all the other values of x . Should one interpret this as indicating an abrupt major change in the form of $\zeta(x)$ very close to the freezing transition? In essence we are faced with the question of whether the Levin or the MCMD estimate is closer to the value of $\Xi(0.7143)$ for the actual system one is attempting to simulate. It should be recalled that the MCMD result was obtained for a system of 5822 hard disks. Finite-size corrections are large and difficult to reliably assess in the immediate vicinity of the freezing transition. No less significant, there is the possibility that for such a large value of x the Levin approximant estimate for Ξ is insufficiently reliable. In the absence of either MCMD data for larger systems or a larger number of known virial coefficients we believe that this issue cannot be resolved at present.

IV. HARD SPHERES

The fluid-solid transition of hard spheres is known¹² to occur for $\rho \approx 0.67\rho_c$. Erpenbeck and Wood² (EW) have generated values of the EOS, with an estimated accuracy of 1 part in 10^4 , for systems consisting of as many as 4000 hard spheres. Applying an extrapolation procedure to their data they were also able to obtain estimates of the EOS of a system of hard spheres appropriate to the thermodynamic limit. Moreover, they succeeded in constructing an analytic expression for $\Xi(\rho)/\rho$, in the form of a $[3/2]$ Padé approximant, which for all practical purposes gives results identical to the data appropriate to the thermodynamic limit. Their final result is given by

$$\Xi(y) = yP_3(y)/Q_2(y), \quad (9)$$

where y is related to the variable $x(=\rho/\rho_c)$, which we are using throughout this work, by $y = \pi(2\sqrt{2})x/3$, and

$$P_3(y) = 1 + 0.055\,567\,82y + 0.013\,944\,51y^2 - 0.001\,339\,96y^3, \quad (10)$$

$$Q_2(y) = 1 - 0.569\,432\,18y + 0.082\,890\,11y^2. \quad (11)$$

A listing of numerical values of Ξ as given by (9) is provided in the second column of Table III. The entry in parentheses is the estimated error when we use linear interpolation between EW's estimated uncertainties in the values of Ξ for the system of 4000 hard spheres.

We have utilized (9)–(11) together with (5) to generate values of ζ versus x for the range $0.42 \leq x \leq 0.63$. The

TABLE III. Values of Ξ for a system of hard spheres: MCMD data of Ref. 2; Eqs. (2)–(4) with $\zeta(x) = 1.435\,44 - 0.102\,83x$.

$x = \rho/\rho_c$	MCMD	Present method
0.10	0.359 43	0.359 43
0.20	0.888 48	0.888 56
0.30	1.682 68	1.683 01
0.40	2.905 37	2.905 93
0.42	3.2237(5)	3.2243
0.43	3.3944(6)	3.3950
0.44	3.5734(6)	3.5739
0.45	3.7611(7)	3.7616
0.46	3.9581(7)	3.9585
0.47	4.1649(7)	4.1652
0.48	4.3820(8)	4.3823
0.49	4.6102(8)	4.6103
0.50	4.8500(9)	4.8500
0.51	5.1022(9)	5.1021
0.52	5.3675(10)	5.3672
0.53	5.6468(11)	5.6464
0.54	5.9410(12)	5.9404
0.55	6.2509(13)	6.2502
0.56	6.5776(13)	6.5768
0.57	6.9223(13)	6.9214
0.58	7.2860(13)	7.2851
0.59	7.6701(13)	7.6693
0.60	8.0760(12)	8.0753
0.61	8.5051(11)	8.5048
0.62	8.9590(10)	8.9593
0.63	9.4395(10)	9.4407

data are presented in Fig. 2. The reason for choosing the first entry for $x=0.42$ is as follows. As remarked in preceding sections, the values of ζ are determined by the discrepancy between the actual EOS and the sum of the

FIG. 2. Data (+) for ζ vs reduced density x for a system of hard spheres upon using Eq. (5) and values of the virial Ξ given by the Erpenbeck-Wood approximant (Ref. 2) [see Eqs. (8)–(10) and the second column of Table III]. A linear least-squares analysis of these data yields $\zeta(x) = 1.435\,44 - 0.102\,83x$, shown as the solid line.

first three terms of the virial series (1). For $x < 0.4$ the relative error in approximating the exact EOS by the first three terms is fairly small. Hence if we were to include MCMD data for Ξ from this regime, even very small uncertainties would be magnified giving rise to large uncertainties in ζ .

A linear least-squares analysis to the data for ζ yields $\zeta_L(x) = \zeta_0 + \zeta_1 x$, where $\zeta_0 = 1.43544(51)$ and $\zeta_1 = -0.10283(85)$. In calculating the estimated error in the values of ζ_0 and ζ_1 we utilized the estimated errors in the values of ζ , obtained using (5) and the estimated errors in Ξ listed in the second column of Table III.

If we consider the full range of the fluid phase, i.e., values of x in the complete interval (0.0, 0.63), $\zeta_L(x)$ provides an approximation to $\zeta(x)$ of only moderate accuracy. Indeed, the data points displayed in Fig. 2 can be viewed as defining a continuous curve with a small, yet nonzero, measure of concavity. Nevertheless, even if we adopt the linear form ζ_L throughout the fluid phase, the resulting error in the values of Ξ is negligibly small. This is because the form of Ξ for small x is essentially insensitive to the detailed form of $\zeta(x)$ in this range.

In the third column of Table III we list the values of Ξ_L , i.e., the representation (2)–(4) in conjunction with the above linear form determined by the linear least-squares analysis. The close agreement between these results and the MCMD data listed in the second column provides strong support for the basic premise of the present work, that $\zeta(x)$ is well approximated by a linear form $\zeta_L(x)$.

The expansion coefficients given by (8) serve as estimates for the scaled virial coefficients B_n^* for $n \geq 5$. More specifically, an estimate of $B_n/(B_2)^{n-1}$ is provided by the quantity $\hat{C}_n/(B_2 \rho_c)^{n-1}$. The latter is given by 0.111 02(2), 0.038 963(2), and 0.012 896(2) for $n = 5, 6$, and

7, respectively, when we use the numerical values of ζ_0 and ζ_1 given above. The best current estimates of these virial coefficients, as obtained via direct calculation,⁷ are listed in Table I. For $n = 5$ these values agree only at the level of 7 parts in 10^3 . Another expression of this fact is that the value $\zeta_0 = 1.43544$ determined above differs from the exact value $\zeta(0) = 1.45152(2)$ by 1%. This discrepancy is considerably larger than what we found for the case of hard disks.

There exist in the literature numerous approximants constructed to represent the EOS of the fluid phase of the hard-sphere system which are based on the higher-order virial coefficients B_5 and B_6 . Most of these are surveyed in Ref. 2. The best existing value⁷ of $B_5/(B_2)^4$ is estimated to have an accuracy of 1 part in 10^5 , whereas for $B_6/(B_2)^5$ the accuracy is only 1 part in 10^2 . Unfortunately very little attention has been paid in the literature to the fact that any approximant for Ξ will necessarily exhibit a large spread in estimates of Ξ for a given value of the density as one varies the value of B_6 within one standard deviation. Furthermore, the relative size of this spread increases very rapidly with increasing density. As a typical example of this strong sensitivity to the uncertainty in B_6 , the Levin T approximant for the hard-sphere system, which uses the virial coefficients through B_6 , yields an estimate for Ξ with an uncertainty of about 2 parts in 10^2 for $x = 0.63$. Virtually all of this large uncertainty is due to the large uncertainty in the current value of B_6 . The very same problem confounds efforts based on Padé approximants or, for that matter, any other technique which explicitly utilizes an estimate of B_6 . We suggest then, that quantitative comparisons between various approximants for the EOS of the hard-sphere system should include a detailed analysis of the uncertainties originating in the uncertainty in the value of B_6 .

TABLE IV. Values of Ξ for a system of hard 4-spheres: present MCMD data; the approximant (2) with $\zeta(x) = 1.2973 - 0.062x$; a modified (Ref. 14) version of the rational approximant of Ref. 13; and the three-term truncated version of the virial series (1).

$x = \rho/\rho_c$	MCMD	Present method	Modified Baus-Colot	Three-term virial series
0.100	0.637 73(28)	0.637 43	0.637 41	0.6350
0.125	0.852 33(42)	0.851 17	0.851 13	0.8452
0.150	1.0922(5)	1.0921	1.0920	1.0792
0.175	1.3643(7)	1.3636	1.3633	1.3390
0.200	1.6701(9)	1.6694	1.6690	1.6262
0.225	2.0147(13)	2.0138	2.0131	1.9424
0.250	2.4015(16)	2.4020	2.4008	2.2895
0.275	2.8404(33)	2.8394	2.8375	2.6691
0.300	3.3319(40)	3.3326	3.3296	3.0829
0.325	3.8821(45)	3.8890	3.8844	3.5326
0.350	4.5197(52)	4.5171	4.5103	4.0201
0.375	5.2309(61)	5.2270	5.2170	4.5468
0.400	6.0399(86)	6.0300	6.0155	5.1147
0.425	6.9364(80)	6.9394	6.9188	5.7253
0.450	7.9714(90)	7.9706	7.9417	6.3804
0.475	9.135(11)	9.1416	9.1015	7.0818
0.500	10.477(12)	10.474	10.418	7.8310

V. HARD 4-SPHERES

The freezing transition for hard 4-spheres has been found³ to occur for $\rho \approx 0.50\rho_c$. In the second column of Table IV we list the best EOS data currently available for a system of 648 particles. The entries shown were generated at the van der Waals Laboratory using the method described in Ref. 3. In particular, periodic boundary conditions have been imposed on the faces of a container in the shape of a 4-cube. The data listed are of greater accuracy and apply to a larger number of densities than that reported previously.³ We have also listed the values of the standard deviation, σ , of Ξ , given by $\sigma \approx 1.2\Xi/\nu^{1/2}$, where ν denotes the number of collisions associated with the MCMD simulations for a given density. The data listed in Table IV have an accuracy of about 1 part in 10^3 . In principle the existing MCMD data for both 4-spheres and 5-spheres should be corrected for the small size of these systems. However, we have not incorporated such corrections since the existing data are characterized by such large statistical uncertainties as to make this tedious task unwarranted.

We have used these EOS data together with (5) to determine values of ζ in the range $0.25 \leq x \leq 0.50$. The data are shown in Fig. 3. As discussed previously for the hard-disk and hard-sphere systems, the avoidance of the low-density regime is due to the large magnification of uncertainties in the MCMD data. A linear least-squares fit to the data for ζ provides the result $\zeta(x) = \zeta_0 + \zeta_1 x$ with $\zeta_0 = 1.2973(59)$ and $\zeta_1 = -0.062(13)$ shown as the solid line in Fig. 3. The estimated errors for ζ_0 and ζ_1 incorporate the estimated errors in the MCMD data. Despite the considerable scatter seen in Fig. 3 we believe that it is fair to state that the data are consistent with a linear dependence of ζ on x . We anticipate that a better linear fit will be possible once EOS data of improved ac-

curacy become available. Combining (2)–(4) together with the linear approximation $\zeta_L(x)$ for $\zeta(x)$ yields values for Ξ which are listed in the third column of Table IV.

Baus and Colot¹³ have presented a rational approximant for the EOS of hard D -spheres, of the form of a polynomial in ρ divided by $(1-\eta)^D$, where η denotes the packing fraction. The quantities η and ρ are related by the relation $\eta = \rho \pi^{D/2} a^D / [2^D \Gamma(1+D/2)]$, where a is the diameter of a hard D -sphere and Γ is the usual gamma function. The degree of the numerator polynomial and its coefficients were determined in terms of known values of the virial coefficients. As such their approximant, in contrast to ours, is free of any adjustable parameters. However, it should be emphasized that the functional form which they selected is *ad hoc* in character. In particular, the choice of the denominator function, which gives rise to an EOS whose radius of convergence corresponds to an unphysical density exceeding the density of closest packing, was¹³ "... inspired by the results of scaled particle theory." Nevertheless, it is noteworthy that when we¹⁴ incorporate the *exact*^{5,6} value of $B_4/(B_2)^3$ within an approximant of the Baus-Colot form we arrive at estimates, given in the fourth column of our Table IV, which are in close agreement with those listed in the third column. As will be seen in Sec. VI, this is not the case for hard 5-spheres.

In the fifth column of Table IV we have listed the results for Ξ obtained using the truncated virial series $\Xi \approx B_2^* x + B_3^* x^2 + B_4^* x^3$. It will be noted that the latter series yields data which already deviate from the MCMD data by more than 1% for $x = 0.15$. The deviation rapidly increases with increasing x . This underscores the obvious, that a knowledge of B_2 , B_3 , and B_4 alone can provide a satisfactory description of the EOS only for very low densities.

VI. HARD 5-SPHERES

The freezing transition for hard 5-spheres has been found³ to occur for $\rho \approx 0.42\rho_c$. The existing EOS data³ for this system were obtained by performing a MCMD study of 512 particles subject to periodic boundary conditions. The results for Ξ (nominal value and standard deviation), are listed in the second column of Table V. Using these values of Ξ together with (5) and the values of the virial coefficients listed in Table I, we obtain the six data points shown in Fig. 4. Invoking a linear least-squares procedure, whereby the same uncertainty is attributed to all values, yields the expression $\zeta_L(x) = \zeta_0 + \zeta_1 x$, with $\zeta_0 = 1.074(16)$ and $\zeta_1 = 0.163(45)$, shown as the solid line in Fig. 4. The quality of the fit is noticeably inferior to that obtained for the values of D considered in the preceding sections. Nevertheless, the value of the linear-correlation coefficient¹⁵ is given by $r = 0.87$, which translates to the fact that there is a probability of about 98% that the six values of ζ are satisfactorily represented by the linear form $\zeta_L(x)$. In defense of the present description we note that the data points are well scattered about the solid line $\zeta_L(x)$, with no apparent trends. We

FIG. 3. Data (+) for ζ vs reduced density x for a system of hard 4-spheres upon using Eq. (5) and MCMD values of the virial Ξ listed in the second column of Table IV. A linear least-squares analysis of these data yields $\zeta(x) = 1.2973 - 0.062x$, shown as the solid line.

TABLE V. Values of Ξ for a system of hard 5-spheres: MCMD data of Ref. 3; the approximant (2) with $\zeta(x)=1.074+0.163x$; a modified (Ref. 16) version of the rational approximant of Ref. 13; and the three-term truncated version of the virial series (1).

$x=\rho/\rho_c$	MCMD	Present method	Modified Baus-Colot	Three-term virial series
0.070 71	0.653(1)	0.6532	0.6530	0.6522
0.10		1.0095	1.0085	1.0052
0.141 42	1.624(3)	1.6183	1.6140	1.6003
0.15		1.7616	1.7562	1.7387
0.20		2.7340	2.7153	2.657
0.212 13	3.008(6)	3.0091	2.9849	2.911
0.25		3.9824	3.9329	3.785
0.26		4.2712	4.2123	4.037
0.27		4.5743	4.5048	4.299
0.282 84	4.997(11)	4.986	4.901	4.650
0.29		5.227	5.131	4.853
0.30		5.577	5.467	5.144
0.31		5.945	5.817	5.446
0.32		6.331	6.184	5.759
0.33		6.736	6.567	6.082
0.34		7.161	6.968	6.415
0.353 55	7.748(16)	7.770	7.540	6.885
0.36		8.073	7.825	7.116
0.37		8.563	8.282	7.483
0.38		9.075	8.760	7.862
0.388 91	9.523(20)	9.553	9.204	8.209
0.406 59	10.589(22)	10.560	10.137	8.926
0.417 19	11.217(24)	11.204	10.732	9.375

therefore are of the opinion that a better fit can be expected once EOS data of improved accuracy become available.

The resulting theoretical results for $\Xi(x)$, as usual obtained by combining (2)–(4) and adopting the above linear approximation $\zeta_L(x)$ to $\zeta(x)$, are listed in the third

column of Table V. The agreement with the MCMD data, given in the second column of the table, is very good even for the highest densities. We believe, then, that adopting a linear approximation for $\zeta(x)$ provides a very satisfactory description of the EOS of this system.

In the fourth column of Table V we list the values of Ξ using a Baus-Colot approximant which we have modified¹⁶ so as to incorporate the exact values of B_2, B_3, B_4 . Note that these results provide an inferior fit to the MCMD data as compared to that offered by our procedure based on a linear approximation to $\zeta(x)$. For the largest density the agreement between the modified Baus-Colot data and the MCMD nominal value is only at the level of 4 parts in 10^2 . Finally, in the fifth column of Table V we list the results for Ξ obtained using the truncated virial series $\Xi \simeq B_2^*x + B_3^*x^2 + B_4^*x^3$. It will be noted that the latter series yields data that already deviate from the MCMD data by more than 3% for $x=0.212$. The deviation rapidly increases with increasing x .

VII. DISCUSSION

The primary, perhaps surprising result of this work is that an accurate representation of the EOS of the fluid phase of systems of hard D -spheres is provided by (2)–(4), together with a linear approximation of $\zeta(x)$, namely $\zeta_L(x)=\zeta_0+\zeta_1x$, for all reduced densities x up to that of the freezing transition. The resulting form of (2) is a rational approximant which utilizes five numbers, the exact values of the three virial coefficients B_2, B_3, B_4 and two constants characterizing the linear function $\zeta_L(x)$. Although the three virial coefficients are characteristics of a

FIG. 4. Data (+) for ζ vs reduced density x for a system of hard 5-spheres upon using Eq. (5) and MCMD values (Ref. 3) of the virial Ξ (second column of Table V). A linear least-squares analysis of these data yields $\zeta(x)=1.074+0.163x$, shown as the solid line.

fluid in the very low-density regime, the remaining two coefficients, defining $\zeta_L(x)$, are apparently sufficient for providing an accurate EOS for densities up to that of the freezing transition.

In this work we have dealt with the cases of $D=2-5$. It is easily seen that the hard rod system ($D=1$) can also be described by (2)–(4). For this system the exact EOS can be written as⁸ $p/(\rho k_B T) - 1 = x/(1-x)$, so that the scaled virial coefficients B_n^* are equal to unity for all n . Equations (2)–(4) then reduce to the exact EOS upon substituting $B_2^* = B_3^* = B_4^* = 1$ and setting $\zeta(x)$ equal to unity for all x , a special case of a linear dependence of ζ on x . Also note that (8) correctly reduces to $\hat{C}_n = 1$ for $n \geq 5$.

A secondary result of the present work is that for the hard-disk and hard-sphere systems the values of the higher-order virial coefficients B_5 , B_6 , and B_7 are rather well approximated using the coefficients $\hat{C}_n$, given by (8), of the power series expansion (7).

We have seen that $\zeta(x)$ appears to be strictly linear throughout the entire fluid regime for the hard-disk system. For the hard-sphere system, $\zeta(x)$ appears to be very nearly linear in the regime (0.42, 0.63). However, upon extrapolating $\zeta_L(x)$ to $x=0$ there is a discrepancy at the level of 1% between $\zeta_L(0) = \zeta_0$ and the exact value of $\zeta(0)$. As we remarked in Sec. IV this is indicative of the fact that $\zeta(x)$ exhibits a small amount of bowing over the range of the fluid phase. This bowing has no practical effect upon the low-density form of Ξ since, as we have repeatedly remarked throughout this work, in the low-density regime the form of $\zeta(x)$ is essentially irrelevant. What requires further study is the detailed behavior of $\zeta(x)$ for the hypersphere systems with $D=4, 5$. The existing EOS data lack sufficient precision, and a major computational effort in this direction is required to ameliorate the situation.

Adopting a linear approximation for $\zeta(x)$ the EOS takes the form of a rational approximant for Ξ , involving the ratio of two polynomials in x of third degree. It should be noted that this rational approximant differs

from the result of approximating (1) by the corresponding Padé approximant, of the form [3/3]. In fact, construction of the [3/3] approximant would require the knowledge of B_2 – B_7 and would not involve any adjustable parameters. Given only three coefficients B_2 , B_3 , and B_4 , the highest-order Padé approximants that can be constructed are of the form [1/2] and [2/1].

Ultimately the goal of statistical mechanics is to establish an EOS for hard D -spheres which is based on first principles. However, approximate treatments such as the present one do serve a useful function in the interim, perhaps providing clues regarding the form of the ultimate theory. In that respect then, the success achieved by adopting a linear approximation for $\zeta(x)$ in the description (2)–(4) serves a useful purpose.

In the Introduction we also remarked that it would be very worthwhile to explore an approach similar to the present one for systems with realistic two-body interatomic and intermolecular potentials. For such systems the calculation of B_2 , B_3 , and B_4 are feasible. The hope would be that the extremely difficult calculations of B_5 and all of the higher-order virial coefficients could be circumvented by adopting a suitable yet simple approximation for $\zeta(x)$. Ideally the resulting EOS would provide an accurate description of a real substance over a wide range of values of density and temperature. We hope to report on this issue in the near future.

ACKNOWLEDGMENTS

It is a pleasure to thank J. J. Erpenbeck for his critical comments, which have led to a greatly improved manuscript. We also wish to thank Marvin Bishop for calling our attention to the article cited in Ref. 13. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. The research performed there was supported in part by the Office of Basic Energy Sciences of the U.S. Department of Energy.

¹J. J. Erpenbeck and M. Luban, Phys. Rev. A **32**, 2920 (1985).

²J. J. Erpenbeck and W. W. Wood, J. Stat. Phys. **35**, 321 (1984); **40**, 787 (1985).

³J. P. J. Michels and N. J. Trappeniers, Phys. Lett. **104A**, 425 (1984).

⁴At the beginning of each of Secs. III–VI we list the main characteristics of the best available EOS data for systems of hard D -spheres with $D=2-5$, respectively.

⁵M. Luban and A. Baram, J. Chem. Phys. **76**, 3233 (1982).

⁶M. Luban and D. L. Pursey (unpublished).

⁷For the hard-disk system the best available estimates for the higher-order virial coefficients have been derived in the following articles for B_5 , B_6 , and B_7 , respectively; K. W. Kratky, J. Stat. Phys. **27**, 533 (1982); **29**, 129 (1982); J. Chem. Phys. **69**, 2251 (1978). The corresponding estimates for hard spheres are also due to Kratky [Physica **87A**, 584 (1977)]. All of these estimates are listed in Table I.

⁸Two exceptional cases are the hard D -sphere systems for

$D=0, 1$. For the first of these systems [M. Luban and A. Baram, J. Phys. A **19**, L585 (1986)] $\Xi(x) = -1 - \ln(1-x)/x$, so that $B_n^* = 1/n$. For the second system [K. F. Herzfeld and M. Goeppert-Mayer, J. Chem. Phys. **2**, 38 (1934); L. Tonks, Phys. Rev. **50**, 955 (1936)] $\Xi(x) = x/(1-x)$, so that $B_n^* = 1$.

⁹The analyticity of $\zeta(x)$ in a region which includes the origin of the x plane follows directly from the assumption that the virial expansion (1) possesses a nonzero radius of convergence.

¹⁰B. J. Alder and T. E. Wainwright, Phys. Rev. **127**, 359 (1962).

¹¹We have chosen to give equal weights to the data for ζ given that there are two different sources for this data. In fact, it is quite difficult to provide a reasonable estimate of the uncertainties for the data that are derived from the Levin T approximant.

¹²B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960).

¹³M. Baus and J. L. Colot, Phys. Rev. A **36**, 3912 (1987).

¹⁴The results for Ξ given in Ref. 13 for hard 4-spheres were ob-

tained using the estimate $B_4/(B_2)^3 \simeq 0.1513(2)$, calculated over two decades ago by Monte Carlo integration methods [F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**, 2048 (1964)]. We find that upon incorporating the exact value of B_4 (Table I, present work) within an approximant of the form proposed by Baus and Colot yields estimates (Table IV, column 4 of the present work) which are substantially closer to the results of the present method than are those reported in Ref. 13 (see their Table VI).

¹⁵See, for example, P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), Sec. 7-1.

¹⁶Baus and Colot (see Ref. 13) have adopted the values

$B_4/(B_2)^3 = 0.0746$ and $B_5/(B_2)^4 = 0.0148$ for hard 5-spheres. These values were obtained by B. C. Freasier and D. J. Isbister [*Mol. Phys.* **42**, 927 (1981)] using Monte Carlo integration methods. In fact, the latter give their results as 0.0746(7) and 0.0148(8), respectively, where their errors are described as constituting two standard deviations from the mean. By contrast, Ree and Hoover (see Ref. 14), also using Monte Carlo methods, obtained $B_4/(B_2)^3 = 0.0761(1)$, which is in excellent agreement with the exact analytical result listed in Table I. The data we list in the fourth column of Table V are obtained using an approximant of the form Z_3 proposed by Baus and Colot, which utilizes values of B_2 , B_3 , and B_4 , but we have substituted the *exact* values of B_2 , B_3 , and B_4 .