

## Virial series for fluids of hard hyperspheres in odd dimensions

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A recently derived method [R. D. Rohrmann and A. Santos, *Phys. Rev. E* **76**, 051202 (2007)] to obtain the exact solution of the Percus–Yevick equation for a fluid of hard spheres in (odd)  $d$  dimensions is used to investigate the convergence properties of the resulting virial series. This is done both for the virial and compressibility routes, in which the virial coefficients  $B_j$  are expressed in terms of the solution of a set of  $(d-1)/2$  coupled algebraic equations which become nonlinear for  $d \geq 5$ . Results have been derived up to  $d=13$ . A confirmation of the alternating character of the series for  $d \geq 5$ , due to the existence of a branch point on the negative real axis, is found and the radius of convergence is explicitly determined for each dimension. The resulting scaled density per dimension  $2\eta^{1/d}$ , where  $\eta$  is the packing fraction, is wholly consistent with the limiting value of 1 for  $d \rightarrow \infty$ . Finally, the values for  $B_j$  predicted by the virial and compressibility routes in the Percus–Yevick approximation are compared with the known exact values [N. Clisby and B. M. McCoy, *J. Stat. Phys.* **122**, 15 (2006)]. © 2008 American Institute of Physics. [DOI: 10.1063/1.2951456]

### I. INTRODUCTION

Interest in studying fluids of hard spheres in  $d$  dimensions goes back at least four decades<sup>1–28</sup> and has recently experienced a new boom.<sup>29–60</sup> The evaluation of virial coefficients, the derivation of the equation of state for these systems, or the determination of the radius of convergence of the virial series are among the issues that have been examined, but many questions related to these issues and others are still open. Providing answers to these questions may shed light on similar issues related to real fluids and therefore efforts in this direction are called for.

The Percus–Yevick (PY) theory<sup>61</sup> is one of the classic integral-equation approximations of liquid-state theory.<sup>62</sup> Apart from yielding the correct expression for the radial distribution function (rdf) to first order in the density (and hence also the correct second and third virial coefficients), its key role in the theory of simple liquids was recognized very early because the resulting integral equation is analytically solvable for the important case of the hard-sphere fluid ( $d=3$ ).<sup>63,64</sup> Furthermore, the approximation provides the exact rdf (although not the exact cavity function inside the core<sup>65</sup>) for hard rods ( $d=1$ ) and has been proven to yield exactly solvable equations in odd  $d$  dimensions.<sup>2,5</sup> In fact, explicit analytical solutions for  $d=5$  and  $d=7$  have been

obtained<sup>2,5,49,57</sup> and, rather recently, numerical solutions for  $d=9$  and  $d=11$  have been reported.<sup>58</sup> These latter have been derived using an alternative method to the one originally employed by Leutheusser<sup>5</sup> which, among other things, allows one to obtain the virial coefficients and the equation of state both from the virial and compressibility routes in a rather straightforward procedure. Also very recently, Adda-Bedia *et al.*<sup>60</sup> have been able to reduce the PY equation for hard disks ( $d=2$ ) to a set of simple integral equations which they then solve numerically. An interesting aspect of this work is their claim that the method may be generalized to any even dimension.

Due to the limited availability of virial coefficients and to the fact that the virial series for high densities relevant to the fluid phase seems to be in general either divergent or slowly convergent, various series convergence accelerating methods, such as Padé or Levin approximants, have been used to derive approximate equations of state for  $d$ -dimensional hard-sphere fluids. However, the radius of convergence of the virial series is not known in general, and hence the usefulness of such approximate equations of state is limited by the uncertainty of its range of applicability. For  $d \leq 3$  all known virial coefficients turn out to be positive but since negative virial coefficients appear for  $d \geq 4$ , the question arises as to whether some higher order virial coefficients both for  $d=2$  and  $d=3$  might eventually become negative.

The main purpose of this paper is to examine the question of convergence of the virial series for fluids of  $d$ -dimensional hard spheres by looking at approximate theories where both the virial coefficients and the equation of state are known. We will use the procedure introduced in

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Ref. 58 to derive the equation of state of the system and the values for the virial coefficients taking both the virial and compressibility routes, all within the PY approximation. In particular, we will investigate the convergence properties of the virial series of the equations of state stemming out of both routes for  $d=5, 7, 9, 11$ , and  $13$  and will show that the radius of convergence is related to a branch point on the negative real axis. Moreover, we will compare the PY virial coefficients with the exact values available in the literature. This comparison suggests that, as the dimensionality increases, the true radius of convergence tends to the value predicted by the PY theory. We will also examine the performance of the compressibility factors obtained from both routes with the corresponding simulation data and will show that the virial series truncated just before the first negative term provides an excellent approximation to the equation of state of the fluid phase.

This paper is organized as follows. In the next section and in order to make the development self-contained, we provide a brief description of the so-called rational function approximation (RFA) approach leading to the PY approximation for fluids of hard hyperspheres in odd dimensions. Section III presents the numerical results of our calculations (together with a comparison with simulation data) for the PY compressibility factors derived via the virial and compressibility routes, respectively, as well as the analysis of the behavior of the PY virial coefficients obtained from the same routes to the equation of state both with respect to the convergence properties of the virial series and with respect to the exact known values. The paper is closed in Sec. IV with some discussion and concluding remarks.

## II. THE PY THEORY

In this section we provide an outline of the main steps leading to the PY approximation for the thermodynamic and structural properties of hard hypersphere fluids in odd dimensions. Instead of following the original derivation by Leutheusser,<sup>5</sup> we will use the RFA method introduced in Ref. 58 which the reader is urged to consult for further details.

### A. General background

We begin by recalling that the static structure factor of a  $d$ -dimensional hard-sphere fluid can be written as

$$S(k) = 1 + \rho \frac{(2\pi)^{(d-1)/2}}{k^{d-2}} i[G(ik) - G(-ik)], \quad (2.1)$$

where  $\rho$  is the particle number density and  $G(s)$  is a Laplace-space functional given by<sup>58</sup>

$$G(s) = \int_0^\infty dr r g(r) \theta_n(sr) e^{-sr}. \quad (2.2)$$

Here  $g(r)$  is the rdf and  $\theta_n(t)$  is the reverse Bessel polynomial of degree  $n \equiv (d-3)/2$ . From these structural functions one may obtain thermodynamic quantities such as the compressibility factor  $Z \equiv p/\rho k_B T$  and the isothermal susceptibility  $\chi \equiv k_B T (\partial \rho / \partial p)_T$ , both defined in terms of the temperature  $T$ , the pressure  $p$ , and the number density  $\rho$  ( $k_B$  being the

Boltzmann constant). The actual relationships read

$$Z = 1 + 2^{d-1} \eta g(\sigma^+) \quad (2.3)$$

and

$$\chi = S(0), \quad (2.4)$$

where  $\sigma$  is the diameter of the particles and  $\eta$  is the packing fraction given by

$$\eta = v_d \rho \sigma^d, \quad v_d = \frac{(\pi/4)^{d/2}}{\Gamma(1+d/2)}, \quad (2.5)$$

where  $v_d$  is the volume of a  $d$  sphere of unit diameter. Henceforth without loss of generality we will set  $\sigma=1$ .

In hard-particle systems, the temperature does not play any relevant role on the structural properties introduced here. Moreover, the thermodynamic state of such fluids can be characterized by a variable alone, say the density or the packing fraction. Therefore, taking into account the thermodynamic relation

$$\chi^{-1} = \frac{\partial}{\partial \eta} (\eta Z), \quad (2.6)$$

the so-called virial equation of state Eq. (2.3) and the compressibility equation of state Eq. (2.4) provide two alternative routes for obtaining the compressibility factor  $Z(\eta)$  of a hard  $d$ -sphere fluid. Since all well-known theoretical methods to obtain structural functions give approximate results (with the exception of the exact solution for the one-dimensional case  $d=1$ ), one typically obtains two approximate solutions: the compressibility factor from the virial route

$$Z_v(\eta) = 1 + 2^{d-1} \eta g_c(\eta), \quad (2.7)$$

with  $g_c(\eta) \equiv g(1^+)$ , and the compressibility factor via the compressibility route

$$Z_c(\eta) = \int_0^1 dx \chi^{-1}(\eta x), \quad (2.8)$$

with  $\chi(\eta)$  given by Eq. (2.4).

For hard-hypersphere fluids in arbitrary odd  $d$  dimensions, the RFA approach provides an analytical representation of the function  $G(s)$  defined by Eq. (2.2) and related to the structure factor Eq. (2.1). In the simplest implementation of the RFA approach, which is the so-called standard RFA and coincides with the PY approximation, the function  $G(s)$  can be written in the explicit form<sup>58</sup>

$$G(s) = \frac{e^{-s}}{s^2} \frac{\sum_{j=0}^{n+1} a_j s^j}{1 + \lambda \eta \sum_{j=0}^{n+1} a_j \phi_{d-j}(s)}, \quad (2.9)$$

with

$$\lambda \equiv (-1)^{(d-1)/2} 2^{d-1} d! \quad !, \quad (2.10)$$

$$\phi_m(s) \equiv \frac{1}{s^m} \left[ \sum_{j=0}^m \frac{(-s)^j}{j!} - e^{-s} \right]. \quad (2.11)$$

The coefficients  $a_j$  are in general functions of the density. Specifically,  $a_0 \equiv (d-2)!!$  and the quantities  $a_j$  with  $j=1, \dots, n+1$  are solutions of the following closed set of  $n+1$  equations:

$$D_{2m+1} - \frac{a_{2m+1}}{(d-2)!!} + \sum_{j=0}^{m-1} \gamma_{2j} D_{2(m-j)-1} = 0, \quad 0 \leq m \leq n, \quad (2.12)$$

with the boundary condition

$$a_j|_{\eta=0} = \frac{(2n+2-j)!}{2^{n+1-j}(n+1-j)!}. \quad (2.13)$$

The coefficients  $D_l$  are linear combinations of the  $\{a_j\}$  given by  $D_0=1$  and

$$D_l = \frac{1}{l!} - \lambda \eta \sum_{m=0}^{n+1} a_m \sum_{j=1}^l \frac{(-1)^{j+d-m}}{(j+d-m)!(l-j)!}, \quad l \geq 1, \quad (2.14)$$

and the quantities  $\gamma_{2m}$  with  $0 \leq m \leq n$  are given in terms of the coefficients  $a_j$  by means of the recursion relation

$$\gamma_{2m} = \frac{a_{2m+2}}{(d-2)!!} - D_{2m+2} - \sum_{j=0}^{m-1} \gamma_{2j} D_{2(m-j)}, \quad 0 \leq m \leq n. \quad (2.15)$$

Here we have adopted the conventions  $a_j=0$  if  $j > n+1$  and  $\sum_{j=0}^m \dots = 0$  if  $m < 0$ . In summary, when the  $\{\gamma_{2m}\}$  obtained from Eq. (2.15) are inserted into Eq. (2.12), and use is made of Eq. (2.14), one gets a closed set of  $n+1=(d-1)/2$  algebraic equations for  $a_1, a_2, \dots, a_{n+1}$ . The number of mathematical solutions (including complex ones) is  $2^n=2^{(d-3)/2}$  and the physical solution is obtained as the one yielding the correct low density limit given by Eq. (2.13).

The contact value of the rdf and the isothermal susceptibility obtained by the PY theory (or, equivalently, by the standard RFA method) are

$$g_c(\eta) = a_{n+1} \left[ 1 + \lambda \eta \sum_{j=0}^{n+1} \frac{(-1)^{d-j}}{(d-j)!} a_j \right]^{-1} \quad (2.16)$$

$$\chi(\eta) = 1 - 2\lambda(d-2)!! \eta \left( D_d + \sum_{j=0}^n \gamma_{2j} D_{d-2-2j} \right), \quad (2.17)$$

with the factors  $D_l$  and  $\gamma_{2m}$  given by Eqs. (2.14) and (2.15), respectively. With these results introduced into Eqs. (2.7) and (2.8) one obtains the compressibility factors  $Z_v(\eta)$  and  $Z_c(\eta)$  as derived within the PY theory from the virial and compressibility routes, respectively.

## B. Virial expansions

The virial expansion of the equation of state is an expansion in powers of the density or the packing fraction,

$$Z(\eta) = 1 + \sum_{j=2}^{\infty} B_j \rho^{j-1} = 1 + \sum_{j=2}^{\infty} b_j \eta^{j-1}, \quad (2.18)$$

and its range of validity is limited by the convergence properties of the series. Notice that

$$b_j = B_j v_d^{1-j}. \quad (2.19)$$

Since  $g_c(\eta=0)=1$ , Eq. (2.3) yields

$$b_2 = 2^{d-1}. \quad (2.20)$$

A more elaborated analysis of the virial equation shows that  $b_3=2^{2d-1}y_1(1)/y_1(0)$ , where  $y_1(r)$  represents the overlap volume of two hyperspheres of unit radius and centers separated by a distance  $r$ . In particular, for  $d$ =odd, one finds<sup>58</sup>

$$b_3 = 2^{2d-1} \left[ 1 - \frac{(2n+3)!!}{2^{n+2}} \sum_{j=0}^{n+1} \frac{(-4)^{-j}}{(2j+1)j!(n+1-j)!} \right]. \quad (2.21)$$

The application of the PY theory yields two virial expansions, one for  $Z_v(\eta)$  and another for  $Z_c(\eta)$ . The virial coefficients in the virial route are given by

$$b_j^{(v)} = \frac{2^{d-1}}{(j-2)!} \partial_{\eta}^{j-2} g_c(\eta)|_{\eta=0}, \quad (2.22)$$

whereas in the compressibility route one has

$$b_j^{(c)} = \frac{1}{j!} \partial_{\eta}^{j-1} \chi^{-1}(\eta)|_{\eta=0}, \quad (2.23)$$

with  $g_c(\eta)$  and  $\chi(\eta)$  given by Eqs. (2.16) and (2.17), respectively, and where  $\partial_{\eta}$  denotes the derivative with respect to  $\eta$ . In practice, what one does is to solve Eq. (2.12) in a recursive way for the coefficients in the density expansion of  $a_1, \dots, a_{n+1}$ . The solutions are exact rational numbers and from them one gets  $b_j^{(v)}$  and  $b_j^{(c)}$  also as exact rational numbers.

## III. RESULTS

In this section, we present the results that follow from the previous derivations. Three aspects will be analyzed. We first deal with the virial coefficients. Then, we examine the issue of the convergence properties of the virial series, and finally, we compare the resulting compressibility factors with simulation data.

### A. Virial coefficients

Because the PY theory is exact to the first order in density, the virial coefficients  $b_2$  and  $b_3$  [Eqs. (2.20) and (2.21)] are exactly reproduced by both routes. Higher virial coefficients are, however, different for each route, as shown in Table I for  $4 \leq j \leq 10$ , where the known exact values are also included for the sake of comparison. The normalized differences  $(b_j^{(v,c)} - b_j)/|b_j|$  between the approximate virial coefficients  $b_j^{(v)}$  and  $b_j^{(c)}$  and the exact values<sup>43,48,59</sup>  $b_j$  are shown in Fig. 1 as functions of the space dimension for  $4 \leq j \leq 10$ . As one can see from the results in this figure, all known (exact) coefficients in  $d=2$  and  $d=3$  lie between  $b_j^{(c)}$  and  $b_j^{(v)}$  in the

TABLE I. Exact and PY values for the virial coefficients  $b_j/b_2^{j-1}$  for  $4 \leq j \leq 10$  and several dimensionalities. The exact values are taken from Refs. 43, 48, and 59, while the PY values for hard disks ( $d=2$ ) are obtained from Ref. 60.

	Exact	PY (v)	PY (c)
$d$	$b_4/b_2^3$	$b_4^{(v)}/b_2^3$	$b_4^{(c)}/b_2^3$
2	0.53223180	0.5008	0.5378
3	0.2869495	0.25	0.296875
5	0.07597248	0.04785156	0.08905029
7	0.00986495	-0.007499695	0.021550816
9	-0.008581	-0.018590778	0.000373515
11	-0.011334	-0.016933400	-0.005004249
13	-0.009523	-0.012604546	-0.005256304
15	-0.006934	-0.008614616	-0.004146893
$d$	$b_5/b_2^4$	$b_5^{(v)}/b_2^4$	$b_5^{(c)}/b_2^4$
2	0.33355604	0.2948	0.3433
3	0.110252	0.0859375	0.12109375
5	0.0129551	0.01294708	0.01638031
7	0.0070724	0.01235023	0.00511681
9	0.007439	0.01172436	0.00404299
11	0.006176	0.00873948	0.00320718
13	0.004307	0.00566100	0.00221818
15	0.002705	0.00337395	0.00138891
$d$	$b_6/b_2^5$	$b_6^{(v)}/b_2^5$	$b_6^{(c)}/b_2^5$
2	0.1988425	0.1667	0.2090
3	0.03888198	0.02734375	0.04492188
5	0.0009815	-0.00286007	0.00145829
7	-0.0035121	-0.00817700	-0.00186533
9	-0.004794	-0.00820391	-0.00229461
11	-0.00395	-0.00583856	-0.00179806
13	-0.002580	-0.00347797	-0.00113940
15	-0.001472	-0.00186395	-0.00063735
$d$	$b_7/b_2^6$	$b_7^{(v)}/b_2^6$	$b_7^{(c)}/b_2^6$
2	0.1148728	0.09194	0.1233
3	0.01302354	0.00830078	0.015625
5	0.0004162	0.00245853	0.00063127
7	0.0025386	0.00655314	0.00138425
9	0.003716	0.00676771	0.00164806
$d$	$b_8/b_2^7$	$b_8^{(v)}/b_2^7$	$b_8^{(c)}/b_2^7$
2	0.0649930	0.04988	0.07107
3	0.0041832	0.00244140	0.00518799
5	-0.0001120	-0.00173717	-0.00022064
7	-0.0019937	-0.00576280	-0.00107878
9	-0.003222	-0.00621239	-0.00133333
$d$	$b_9/b_2^8$	$b_9^{(v)}/b_2^8$	$b_9^{(c)}/b_2^8$
2	0.0362193	0.02677	0.04025
3	0.0013094	0.00070190	0.00166321
5	0.0000747	0.00134572	0.00017676
7	0.0016869	0.00542528	0.00091218
9	0.003029	0.00615464	0.00117921
$d$	$b_{10}/b_2^9$	$b_{10}^{(v)}/b_2^9$	$b_{10}^{(c)}/b_2^9$
2	0.0199537	0.01424	0.02248
3	0.0004035	0.00019836	0.00051880
5	-0.0000492	-0.00108546	-0.00012788
7	-0.001514	-0.00537523	-0.00081922
9	-0.00306	-0.00645733	-0.00111652

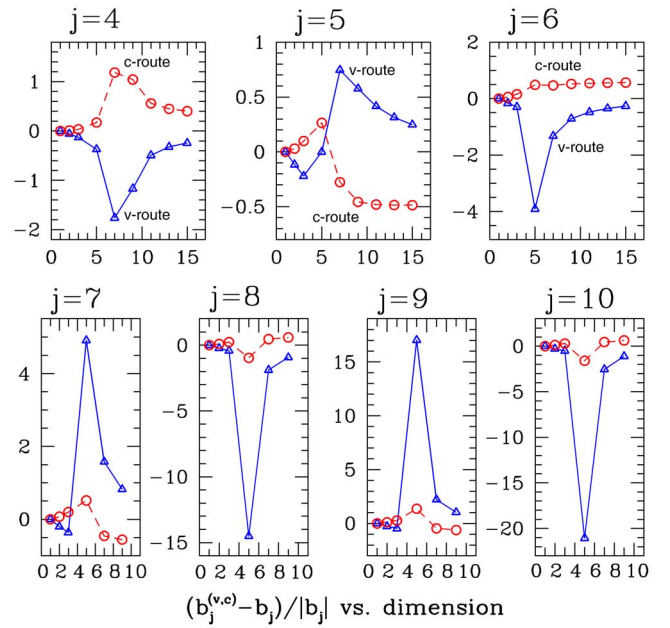


FIG. 1. (Color online) Normalized differences between the virial coefficients  $b_j^{(v)}$  (triangles) and  $b_j^{(c)}$  (circles) and the exact values (Refs. 43, 48, and 59)  $b_j$  as functions of the space dimension for  $4 \leq j \leq 10$ . The data for  $d=2$  have been obtained from Ref. 60. The lines have been drawn to guide the eye.

form  $b_j^{(v)} < b_j < b_j^{(c)}$ , but this is not so in higher dimensions. A transition behavior seems to take place at  $d=5$  since in that case one has  $b_j < b_j^{(c)} < b_j^{(v)}$  for  $j=7$  and 9, while  $b_j > b_j^{(c)} > b_j^{(v)}$  for  $j=8$  and 10. For  $d \geq 7$ , however, the trends seem to be  $b_j^{(v)} < b_j < b_j^{(c)}$  for  $j=\text{even} \geq 4$  and  $b_j^{(c)} < b_j < b_j^{(v)}$  for  $j=\text{odd} \geq 5$ . The top panels of Fig. 1 seem to indicate that the relative deviations of the PY values with respect to the exact ones tend to decrease and stabilize with increasing  $d$ , especially in the case of  $b_j^{(c)}$ . Of course, a confirmation of all these trends would require the knowledge of the exact virial coefficients for higher orders  $j$  and higher dimensionalities  $d$ . The fact that  $b_4^{(v)} < b_4 < b_4^{(c)}$  for all  $d$  implies that  $Z_v(\eta) < Z(\eta) < Z_c(\eta)$  for asymptotically low densities. On the other hand, since both  $Z_v(\eta)$  and  $Z_c(\eta)$  are  $\leq 1$  for any  $\eta < 1$ ,<sup>58</sup> i.e., even for densities higher than the close-packing value  $\eta_{\text{cp}}$ , it can be reasonably expected that  $Z(\eta) > Z_c(\eta) > Z_v(\eta)$  beyond a certain density, although this possibly happens in the metastable region. A precursor of this effect might be the relation of  $b_5^{(c)} < b_5 < b_5^{(v)}$  for  $d \geq 7$ .

The assessment of the performance of the PY virial coefficients with respect to the exact results may also profit from a different representation of the data. This is shown in the four panels of Fig. 2, where we have plotted the ratio  $b_2 b_{j-1} / b_j$  as a function of  $j$  for  $3 \leq j \leq 20$  (with both  $b_j^{(v)}$  and  $b_j^{(c)}$  and the values from Refs. 43, 48, and 59) for  $d=2, 3, 5, 7$ , and 9. As we will discuss below, the magnitude of this ratio is related to the radius of convergence of the virial series. In this instance, the regularity of the results for the lower  $j$ 's observed for  $d=2$  and  $d=3$  is lost in higher dimensions. It is interesting to note that for  $d=7$  and 9 the exact values of  $b_2 b_{j-1} / b_j$  for the higher  $j$ 's ( $7 \leq j \leq 10$ ) lie very

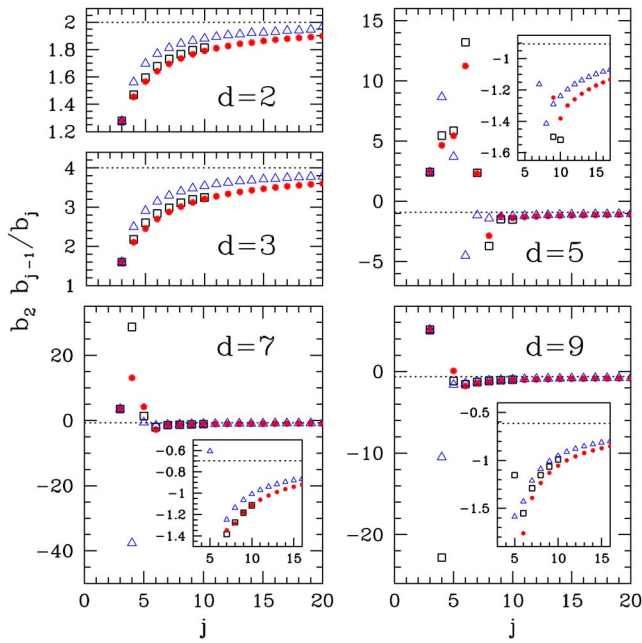


FIG. 2. (Color online) Ratio  $b_2 b_{j-1}/b_j$  as a function of  $j$  for  $3 \leq j \leq 20$  and  $d=2, 3, 5, 7,$  and  $9$ ;  $b_j^{(v)}$  (triangles),  $b_j^{(c)}$  (circles), and the exact values (Refs. 43, 48, and 59)  $b_j$  (squares). The dash-dotted line is the limiting value of this ratio for both PY virial coefficients when  $j \rightarrow \infty$ . The insets in the cases  $d=5, 7,$  and  $9$  show in more detail how the limiting value is approached.

close to the PY values. Whether this good agreement is accidental or not cannot be assessed before exact values of  $b_j$  for  $j \geq 11$  and/or  $d \geq 11$  are known.

## B. Radius of convergence of the virial series

Now we turn to the question of the convergence properties of the virial series. The radius of convergence of the virial series for each dimension  $d$ ,  $\eta_0 = \lim_{j \rightarrow \infty} |b_{j-1}/b_j|$ , is determined by the modulus of the singularity of  $Z(\eta)$  closest to the origin in the complex  $\eta$  plane. In order to inhibit the influence of  $d$  on the characteristic density values, we will sometimes choose  $b_2 \eta$  (rather than  $\eta$  or  $\rho \sigma^d$ ) to measure the density. In Fig. 3 we display the PY compressibility factor  $Z_v(\eta)$  as a function of  $b_2 \eta$  for  $d=5, 7, 9,$  and  $11$ . In the figure, apart from showing  $Z_v(\eta)$  in the physical domain of positive densities (thick solid line, shaded region), we have provided its analytic continuation to negative values of  $\eta$ . The thin solid line shows such a continuation. It turns out that there exists a certain negative value  $\eta = -\eta_0$  such that  $Z_v(\eta)$  keeps being real in the interval  $-\eta_0 < \eta < 0$ . However, at  $\eta = -\eta_0$   $Z_v(\eta)$  merges with an unphysical root (dashed line) and both roots become a pair of complex conjugates for  $\eta < -\eta_0$  (the two dotted lines represent their imaginary parts). This shows that  $Z_v(\eta)$ , as well as  $Z_c(\eta)$ , possesses a branch point at  $\eta = -\eta_0$ . This is the singularity on the real axis closest to the origin. If no other singularity lying in the complex plane is closer to the origin, then  $\eta_0$  is the radius of convergence of the series. Figure 4 provides the radius of convergence of the virial series for  $Z_v(\eta)$  and  $Z_c(\eta)$ , this time by representing again  $b_2 b_{j-1}^{(v,c)}/b_j^{(v,c)}$  as a function of  $j$  for  $3 \leq j \leq 150$  and  $d=3, 5, 7, 9, 11,$  and  $13$ . As is well known, the radius of convergence predicted by the PY theory is  $\eta_0 = 1$

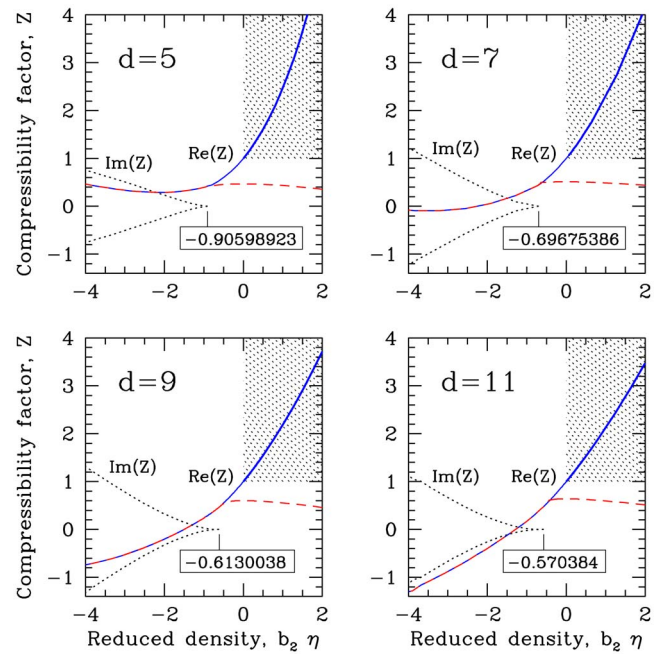


FIG. 3. (Color online) Compressibility factor  $Z_v(\eta)$  in the physical domain of positive densities (thick solid line and shaded region) and its analytic continuation for  $\eta < 0$  (thin solid line) as a function of  $b_2 \eta$  for  $d=5, 7, 9,$  and  $11$ . At the negative value  $\eta = -\eta_0$   $Z_v(\eta)$  merges with an unphysical real root (dashed line) and both roots become a pair of complex conjugates for  $\eta < -\eta_0$  whose imaginary parts are represented by the two dotted lines. The boxed numbers are the corresponding values of  $-b_2 \eta_0$ .

for  $d=3$ . On the other hand, for  $d \geq 5$  the radius of convergence is  $\eta_0 < 1$  and coincides with the value  $\eta_0$  corresponding to the branch point on the negative real axis shown in Fig. 3. The values of  $\eta_0$ ,  $b_2 \eta_0$ , and of the scaled density per dimension<sup>13</sup>  $\hat{\rho}_0 = 2\eta_0^{1/d}$  are shown in Table II for odd dimensions in the interval  $3 \leq d \leq 13$ . It can be observed that the values of  $\hat{\rho}_0$  are consistent with the limit  $\hat{\rho}_0 \rightarrow 1$  as  $d \rightarrow \infty$  conjectured by Frisch and Percus.<sup>13</sup> This agreement, along with the behavior observed in Fig. 2, supports the reliability of the radius of convergence predicted by the PY theory, at least for high dimensions.

## C. Compressibility factors

We now turn to the compressibility factor. In Fig. 5, we present a comparison between the PY values for  $Z_v(\eta)$  and  $Z_c(\eta)$  and some of the available simulation data<sup>6,21,49,51,53,54,56,59,66,67</sup> for various dimensions. It follows from this figure that as  $d$  increases,  $Z_c(\eta)$  becomes a rather accurate approximation for the simulation results. Note, however, that the simulation data for  $d=9$  are restricted to the density region where  $Z_v(\eta) \approx Z_c(\eta)$ .

Comparison between the density range in Fig. 5 and the values of  $\eta_0$  tabulated in Table II shows that the good agreement between  $Z_c$  and  $Z$  for  $d=5$  and  $d=7$  extends to  $\eta > \eta_0$ , i.e., well beyond the radius of convergence of  $Z_v$  and  $Z_c$ . This might cast doubts on the practical usefulness of the virial coefficients to predict the equation of state of hard hyperspheres in the fluid region with  $\eta > \eta_0$ . However, as the following discussion shows, we have observed that this is not the case. Let us denote by  $j^*$  the order of the virial coef-

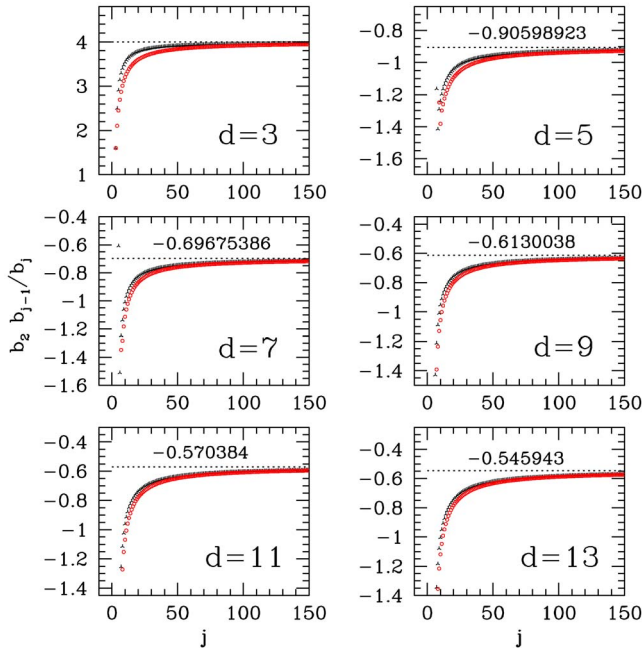


FIG. 4. (Color online) Ratio  $b_2 b_{j-1}/b_j$  as a function of  $j$  for  $3 \leq j \leq 150$  and  $d=3, 5, 7, 9, 11,$  and  $13$ ,  $b_j^{(v)}$  (triangles), and  $b_j^{(c)}$  (circles). The dash-dotted line is the limiting value of this ratio for both PY virial coefficients when  $j \rightarrow \infty$ , and from such value one can immediately get the radius of convergence of the virial series.

ficient preceding the first negative coefficient, i.e.,  $b_j > 0$  for  $j \leq j^*$  but  $b_{j+1} < 0$ . Analogously one can define  $j_v^*$  and  $j_c^*$  in connection with  $b_j^{(v)}$  and  $b_j^{(c)}$ , respectively. For instance, at  $d=5$  one has (see Table I)  $j^* = j_c^* = 8$  and  $j_v^* = 6$ , while  $j^* = j_c^* = 6$  and  $j_v^* = 4$  at  $d=7$ . Let us now define the *truncated* virial series

$$Z^*(\eta) = 1 + \sum_{j=2}^{j^*} b_j \eta^{j-1}, \quad (3.1)$$

with similar definitions of  $Z_v^*(\eta)$  and  $Z_c^*(\eta)$ . Since the first neglected term is negative, it follows that, at least for low densities,  $Z^*(\eta)$ ,  $Z_v^*(\eta)$ , and  $Z_c^*(\eta)$  are upper bounds of  $Z(\eta)$ ,  $Z_v(\eta)$ , and  $Z_c(\eta)$ , respectively. Furthermore, we have checked (for  $d=5, 7, 9, 11,$  and  $13$ ) that  $Z_v^*(\eta)$  and  $Z_c^*(\eta)$  are excellent estimates of  $Z_v(\eta)$  and  $Z_c(\eta)$ , respectively, much better in the region  $\eta > \eta_0$  than any other truncated virial series. Does this property extend to  $Z^*(\eta)$  as well? Comparison between  $Z^*(\eta)$  and simulation data of  $Z(\eta)$  for  $d=5$  and  $7$  indicates that this is indeed the case. In Fig. 6, we have represented the approximate compressibility factors  $Z_v^*(\eta)$ ,  $Z_c^*(\eta)$ , and  $Z^*(\eta)$  for  $d=5$  and  $7$ , and compared such approximations with simulation values.<sup>21,49,67</sup> Again the superiority of the approximate PY compressibility factor obtained via the compressibility route over the one obtained via the virial route is apparent. More interesting, however, is the fact that if one considers the similar approximation  $Z^*(\eta)$  (i.e., using the exact virial coefficients), the agreement between this approximation and the simulation data is strikingly good over the whole fluid phase region where these data are available, especially in the case of  $d=5$ . In fact, since as already pointed out, the PY theory leads to the exact (positive)  $b_2$

TABLE II. The radius of convergence  $\eta_0$  of the virial series in the PY theory, and the associated quantities  $b_2 \eta_0$  and  $\hat{\rho}_0 = 2 \eta_0^{1/d}$  for fluids at  $d=3, 5, 7, 9, 11,$  and  $13$ .

$d$	$\eta_0$	$b_2 \eta_0$	$\hat{\rho}_0$
3	1	4	1.58740105
5	0.056624327	0.90598923	1.12623911
7	0.010886779	0.69675386	1.04854495
9	0.002394546	0.6130038	1.02289857
11	0.000557016	0.570384	1.01204491
13	0.000133287	0.545943	1.00678503

and  $b_3$  (irrespective of whether one takes the virial or the compressibility routes) given that. Since for  $d \geq 9$  both the exact fourth virial coefficient and the PY  $b_4^{(v)}$  are negative, it turns out that these dimensions  $j^* = j_v^* = 3$  and the truncated expansions  $Z^*(\eta) = Z_v^*(\eta) = 1 + b_2 \eta + b_3 \eta^2$  coincide. Furthermore, since the PY coefficient  $b_4^{(c)}$  also becomes negative for  $d \geq 11$ , all three truncated expansions for the compressibility factor become the same for  $d \geq 11$ .

## IV. DISCUSSION

The preceding results lend themselves to further consideration. One might have reasonably wondered whether the trend observed for all the known virial coefficients  $b_j$  both in  $d=2$  and  $d=3$ , namely the fact that they are bracketed by  $b_j^{(v)}$  and  $b_j^{(c)}$ , would remain valid for all virial coefficients in these dimensions and also hold for the higher dimensions. The following reasoning indicates that for any  $d > 1$  there must be at least one virial coefficient that does not comply with the above trend. Since both  $Z_v(\eta)$  and  $Z_c(\eta)$  only diverge for  $\eta=1$  and the true  $Z(\eta)$  must have a divergence at the close-

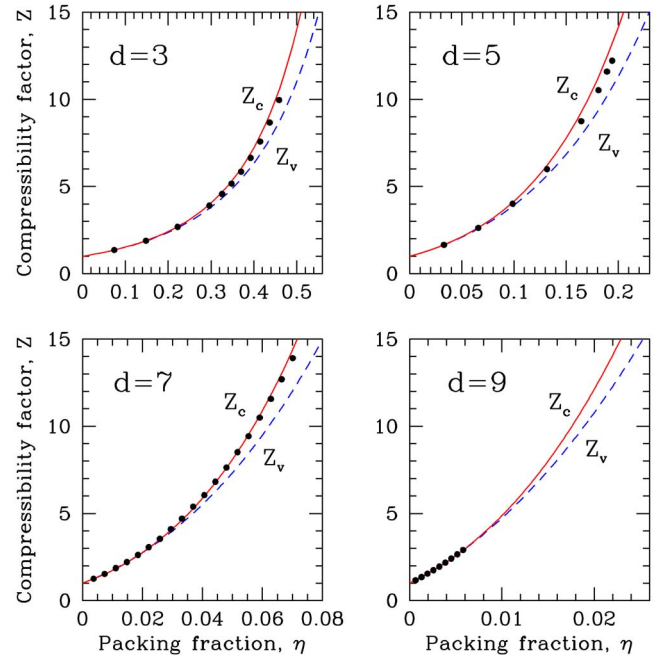


FIG. 5. (Color online) Compressibility factors  $Z_v(\eta)$  (dashed line) and  $Z_c(\eta)$  (continuous line) of the PY theory as functions of the packing fraction  $\eta$  for  $d=3, 5, 7,$  and  $9$ , and simulation data (Refs. 21, 49, 59, 66, and 67) (filled circles).

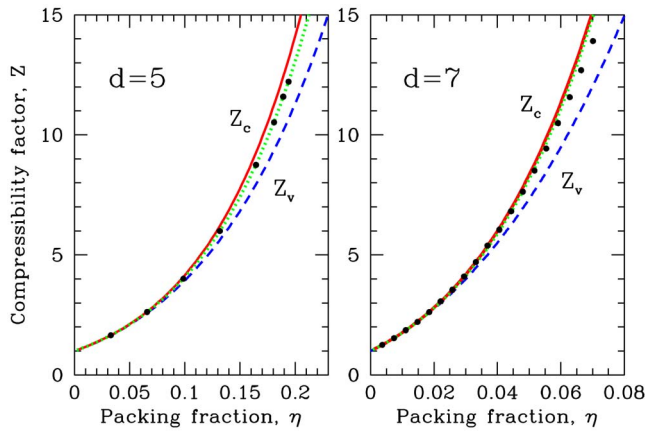


FIG. 6. (Color online) Truncated approximations  $Z_v^*(\eta)$  (dashed line),  $Z_c^*(\eta)$  (continuous line), and  $Z^*(\eta)$  (dotted line) as functions of the packing fraction  $\eta$  for  $d=5$  and 7, and simulation data (Refs. 21, 49, and 67) (filled circles).

packing fraction  $\eta_{cp} < 1$ , then at a smaller packing fraction (although possibly in the metastable fluid region),  $Z(\eta)$  must lie above  $Z_v(\eta)$  and  $Z_c(\eta)$ . This crossing should manifest itself in the behavior of the virial coefficients even if the radius of convergence of the virial series is smaller (or very much smaller) than the packing fraction at which the crossing occurs. According to our findings, the bracketing  $b_j^{(v)} < b_j < b_j^{(c)}$  is lost already for  $b_5$  at  $d=7$ , where one has  $b_j^{(c)} < b_j < b_j^{(v)}$ , and it seems that this will happen for all higher odd  $j$ 's but not for even ones. We also find that the relative deviations of the PY virial coefficients with respect to the true coefficients tend to stabilize with increasing dimensionality.

Concerning the radius of convergence of the virial series, two key aspects should be pointed out. The first one is that, as our present results clearly confirm, in the PY theory and for  $d \geq 5$  the singularity closest to the origin is a branch point located on the negative real axis and corresponds to a packing fraction  $\eta_0$  much smaller than the one delimiting the fluid phase region. The second observation is that the PY values for the ratio  $b_2 b_{j-1} / b_j$  for the higher  $j$ 's lie very close to the exact values. Furthermore, the resulting scaled density per dimension  $\hat{\rho}_0$  is wholly consistent with the limiting value of one for  $d \rightarrow \infty$ . Hence, on one hand, the scenario of an alternating series for the true virial series by Clisby and McCoy<sup>48</sup> (perhaps even for  $d=3$ ) is reinforced and, on the other, one may conjecture that its radius of convergence will also be close to the one in the PY theory. In connection with the latter point it is instructive to compare the PY values of the radius of convergence  $\eta_0$  with known bounds. In 1964, Lebowitz and Penrose<sup>68</sup> derived the lower bound  $b_2 \eta_0 \geq 0.07238$ , which is clearly verified by the values of Table II. They also showed that no phase transitions exist for values of  $b_2 \eta$  less than  $1/2(1+e) \approx 0.135$ , which is again consistent with the PY predictions for  $\eta_0$  and the scenario<sup>48</sup> of a leading singularity on the positive real axis at the freezing density  $\eta_f > \eta_0$ . Recently, Clisby and McCoy<sup>43</sup> estimated the value  $b_2 \eta = 0.5$  for the radius of convergence of the sum of the Ree–Hoover diagrams. It is quite interesting to notice that

the values of  $b_2 \eta_0$  predicted by the PY approximation (see Table II) seem to tend from above precisely to 0.5, i.e.,  $\lim_{d \rightarrow \infty} b_2 \eta_0 = 0.5$ .

As a final point, it is worth mentioning that the regularity observed for the ratio  $(Z_v - Z)/(Z_c - Z_v)$  in  $d=3$  and  $d=5$ , which leads to the Carnahan–Starling<sup>69</sup> equation of state in the former case and something similar in the latter,<sup>35</sup> seems not to hold for  $d=7$ , even if the low density values (which are subjected to great uncertainties) are ignored. The recent simulation data of Bishop *et al.*<sup>59</sup> are also for low density and with error bars comparable to  $Z_c - Z_v$  so that further conclusions on this matter are precluded at this stage.

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