



Virial coefficients and equations of state for mixtures of hard discs, hard spheres and hard hyperspheres

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The composition-independent virial coefficients of a d -dimensional binary mixture of (additive) hard hyperspheres following from a recent proposal for the equation of state of the mixture (SANTOS, A., YUSTE, S. B., and LÓPEZ DE HARO, M., 1999, *Molec. Phys.*, **96**, 1) are examined. Good agreement between theoretical estimates and available exact or numerical results is found for $d = 2, 3, 4$ and 5 , except for mixtures whose components are very disparate in size. A slight modification that remedies this deficiency is introduced and the resummation of the associated virial series is carried out, leading to a new proposal for the equation of state. The case of binary hard sphere mixtures ($d = 3$) is analysed in some detail.

1. Introduction

Depending on the nature of the independent variables, it is well known that the full thermodynamic description of a given system requires the availability of either one of the thermodynamic potentials or of the corresponding equations of state. In the case of classical fluids, the usual expression for the equation of state (EOS) is a relationship between the pressure p , the density ρ and the temperature T of the fluid. However, except for very few ideal systems, the explicit (exact) form of this relationship is not known in general. Therefore, given the fact that an experimental determination of the EOS for every particular fluid of course is not practical, researchers have concentrated their efforts on proposing ‘reasonable’ empirical or semi-empirical approximations. Perhaps the neatest example of such an approach, produced over a century ago and providing an essentially correct qualitative picture of the thermodynamic properties of gases and liquids, is the celebrated van der Waals EOS [1]. An alternative proposal, first introduced by Kammerlingh Onnes [2] as a mathematical representation of experimental results on the equation of state of gases and liquids, is the so called virial equation of state. Written for the compressibility factor $Z \equiv p/\rho k_B T$ (where k_B is the Boltzmann constant)

as a power series in ρ , it provides an expansion that gives the deviation from ideal gas behaviour in ascending powers of the density, namely

$$Z = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1}. \quad (1)$$

Here, the B_n are the virial coefficients. For a simple fluid, the virial coefficients are in general functions of T alone, while in the case of mixtures they also depend on composition [3]. An interesting aspect of the virial equation of state, discovered many years after it was introduced, is the fact that it can be derived rigorously using statistical mechanics [4]. This in turn implies that the virial coefficients are not merely empirical constants but rather are related to intermolecular interactions in a well defined manner. It is unfortunate, however, that in general the actual computation of the virial coefficients is a formidable task, and that the radius of convergence of the series in equation (1) is not known.

In the case of hard core fluids (rods, discs, spheres and hyperspheres) the virial coefficients are easier to compute than those corresponding to any other intermolecular interactions. Even in these model systems and with the exception of hard rods, where the exact EOS and corresponding virial coefficients are known, only the first few of such coefficients are available so far [5–8] because the number of cluster integrals involved increases very rapidly with the order of the coefficient. The availability is scarcer for mixtures than for simple fluids, although recently there has been renewed interest

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in partially remedying this deficiency [9–19]. The limited knowledge of the virial coefficients has proved useful, however, in the sense that proposals for the EOS of these systems may be judged, among other things, by how well the virial coefficients arising in such proposals compare with the exact values. The rationale here is that a ‘good’ theoretical EOS should lead to an accurate prediction of the value of the virial coefficients. Alternatively, the few available virial coefficients may also be used profitably to construct a rational (Padé or Levin) [6, 20–24] approximation to the EOS, or to guide in the construction of a theoretical EOS, as was the case with the Carnahan–Starling (CS) EOS [25] for a simple hard sphere fluid.

A variety of (approximate) EOSs for simple fluids composed of hard discs and hard spheres are available in the literature [26], and some work has also been reported on simple fluids of hard hyperspheres [27–31]. Very recently we introduced a simple recipe to derive the compressibility factor of a multicomponent mixture of d -dimensional hard hyperspheres in terms of that of the corresponding single-component system [32]. A straightforward consequence of such a recipe is that one can readily derive the explicit expressions for the virial coefficients of the mixture in terms of those of the single-component fluid for all d . The major aim of this paper is to assess the usefulness of our recipe further by comparing the predictions of the values of the virial coefficients of binary mixtures of hard discs, hard spheres and hard hyperspheres for $d=4$ and $d=5$ with those obtained through Monte Carlo integration. Along the way we will introduce slight modifications to our original proposal and consider an alternative EOS to cope with mixtures of components very disparate in size. This new EOS is consistent with the forms suggested by Wheatley for the virial coefficients of hard discs [33] and hard spheres [34].

2. Approximate equation of state and virial coefficients for a binary mixture of d -dimensional hard spheres

In this section we consider first a multicomponent mixture of d -dimensional (additive) hard hyperspheres, and then restrict ourselves to *binary* mixtures of hard hyperspheres in d dimensions.

Let the number of components be N , the total number density of the mixture be ρ , the set of mole fractions be $\{x_i\}$, and the set of diameters be $\{\sigma_i\}$, ($i = 1, 2, \dots, N$). The packing fraction is $\eta = \sum_{i=1}^N \eta_i = v_d \rho \langle \sigma^d \rangle$, where $\eta_i = v_d \rho_i \sigma_i^d$ is the partial packing fraction due to the species i , $\rho_i = \rho x_i$ is the partial number density corresponding to species i , $v_d = (\pi/4)^{d/2} / \Gamma(1 + d/2)$ is the volume of a d -dimensional sphere of unit diameter and $\langle \sigma^n \rangle \equiv \sum_{i=1}^N x_i \sigma_i^n$. In previous work [32] we proposed a simple equation of state for the mixture, $Z_m(\eta)$, consis-

tent with a given EOS for a single component system, $Z_s(\eta)$, at the same packing fraction η , namely

$$Z_m(\eta) = 1 + [Z_s(\eta) - 1] 2^{1-d} \Delta_0 + \frac{\eta}{1-\eta} (1 - \Delta_0 + \frac{1}{2} \Delta_1), \quad (2)$$

with

$$\Delta_p \equiv \frac{\langle \sigma^{d+p-1} \rangle}{\langle \sigma^d \rangle^2} \sum_{m=p}^{d-1} \frac{(d+p-1)!}{m!(d+p-1-m)!} \langle \sigma^{m-p+1} \rangle \langle \sigma^{d-m} \rangle. \quad (3)$$

In the 1-dimensional case, equation (2) yields the *exact* result $Z_m(\eta) = Z_s(\eta)$. Further, for binary mixtures with $d = 2, 3, 4$ and 5 , it proved to be very satisfactory when a reasonably accurate $Z_s(\eta)$ was taken [24, 32, 35, 36].

From the virial expansion $Z_s(\eta) = 1 + \sum_{n=2}^{\infty} b_n \eta^{n-1}$, where b_n are (reduced) virial coefficients, and according to equations (1)–(3), the n th virial coefficient of the mixture is given by

$$B_n = v_d^{n-1} \langle \sigma^d \rangle^{n-1} (2^{1-d} \Delta_0 b_n + 1 - \Delta_0 + \frac{1}{2} \Delta_1), \quad (4)$$

and explicitly for $n \geq 2$

$$B_n = v_d^{n-1} \langle \sigma^d \rangle^{n-3} \sum_{m=0}^d \frac{(d-1)!}{m!(d-m)!} \langle \sigma^{d-m} \rangle \times \left[(2^{1-d} b_n - 1)(d-m) \langle \sigma^{m+1} \rangle \langle \sigma^{d-1} \rangle + \frac{d}{2} \langle \sigma^m \rangle \langle \sigma^d \rangle \right]. \quad (5)$$

Now we shall look specifically at *binary* mixtures. In this case it is useful to define composition-independent coefficients B_{n_1, n_2} as

$$B_n = \sum_{n_1=0}^n B_{n_1, n-n_1} \frac{n!}{n_1!(n-n_1)!} x_1^{n_1} x_2^{n-n_1}. \quad (6)$$

Our objective is to use our model to get approximate expressions for B_{n_1, n_2} as explicit functions of σ_1 , σ_2 , and d . In appendix A it is shown that the result is

$$B_{n_1, n_2} = v_d^{n-1} \sigma_1^{d(n-1)} \alpha^{d(n_2-1)} [C_{n_1, n_2}^{(1)} \alpha^d + C_{n_1, n_2}^{(2)} \alpha^{d-1} + C_{n_1, n_2}^{(3)} (1 + \alpha)^{d-1} + C_{n_2, n_1}^{(3)} \alpha (1 + \alpha)^{d-1} + C_{n_2, n_1}^{(2)} \alpha + C_{n_2, n_1}^{(1)}], \quad (7)$$

where $n \equiv n_1 + n_2$, $\alpha \equiv \sigma_2 / \sigma_1$ and

$$C_{n_1, n_2}^{(1)} = \frac{n_1(n_1 - 1)[(n_1 - 2)b_n + 2^{d-1}n_2]}{n(n-1)(n-2)}, \quad (8)$$

$$C_{n_1, n_2}^{(2)} = \frac{n_1 n_2 (n_1 - 1)(b_n - 2^{d-1})}{n(n-1)(n-2)}, \quad (9)$$

$$C_{n_1, n_2}^{(3)} = \frac{n_1 n_2 [(n_2 - 1)2^{d-1}b_n + n_1 - n_2]}{n(n-1)(n-2)}. \quad (10)$$

The special case of $n = 2$ is obtained by first setting $b_n = 2^{d-1}$ and then setting $n = 2$. The result is

$$C_{n_1, n_2}^{(1)} = 2^{d-2}n_1(n_1 - 1), \quad C_{n_1, n_2}^{(2)} = 0, \quad C_{n_1, n_2}^{(3)} = \frac{1}{2}n_1 n_2. \quad (11)$$

This gives the *exact* second virial coefficient.

Equation (7) expresses the reduced coefficient.

$$B_{n_1, n_2}^*(\alpha) \equiv B_{n_1, n_2}(\sigma_1, \sigma_2) \sigma_1^{-d(n-1)} \alpha^{-d(n_2-1)} \quad (12)$$

as a polynomial in α of degree d . Although it is known that the exact coefficients do not have in general such a polynomial structure [34], most of the proposals to date for $d = 2$ and $d = 3$ are polynomials [15, 16, 18, 23, 24, 33, 34]. Let us see which consistency conditions the approximations (7)–(10) fulfil. First, they verify the obvious symmetry property $B_{n_1, n_2}(\sigma_1, \sigma_2) = B_{n_2, n_1}(\sigma_2, \sigma_1)$, which implies that $B_{n_1, n_2}^*(\alpha) = \alpha^d B_{n_2, n_1}^*(1/\alpha)$. In addition, the coefficients (8)–(10) satisfy the properties

$$C_{n_1, n_2}^{(1)} + C_{n_2, n_1}^{(2)} + 2^{d-1} C_{n_2, n_1}^{(3)} = \frac{n_1}{n} b_n, \quad (13)$$

$$dC_{n_1, n_2}^{(1)} + (d-2)C_{n_1, n_2}^{(2)} + 2^{d-1} C_{n_2, n_1}^{(3)} = \frac{n_1}{n(n-1)} [2^{d-1} n_2 + d(n_1 - 1)b_n], \quad (14)$$

$$C_{n,0}^{(1)} = b_n, \quad C_{0,n}^{(1)} = C_{n,0}^{(2)} = C_{0,n}^{(2)} = C_{n,0}^{(3)} = C_{0,n}^{(3)} = 0. \quad (15)$$

Equation (13) implies that

$$C_{n_1, n_2}^{(1)} + C_{n_2, n_1}^{(1)} + C_{n_1, n_2}^{(2)} + C_{n_2, n_1}^{(2)} + 2^{d-1} [C_{n_1, n_2}^{(3)} + C_{n_2, n_1}^{(3)}] = b_n, \quad (16)$$

which guarantees that

$$B_{n_1, n_2}^*(\alpha = 1) = v_d^{n-1} b_n, \quad (17)$$

i.e. if both species have the same size we recover the one-component case. The same situation appears if $x_1 = 0$ or $x_2 = 0$, which means that $B_{n,0}^*(\alpha) = v_d^{n-1} b_n \alpha^d$ and $B_{0,n}^*(\alpha) = v_d^{n-1} b_n$. This is verified as a consequence of equation (15). A subtler consistency condition is [34]

$$\left. \frac{\partial B_{n_1, n_2}^*}{\partial \alpha} \right|_{\alpha=1} = d \frac{n_1}{n} v_d^{n-1} b_n, \quad (18)$$

which ensures that the derivative of the excess free energy of mixing with respect to σ_2 is zero when the

spheres are of the same size [34]. In approximation (7), equation (18) requires

$$dC_{n_1, n_2}^{(1)} + (d-1)C_{n_1, n_2}^{(2)} + 2^{d-2}(d-1)C_{n_1, n_2}^{(3)} + 2^{d-2}(d+1)C_{n_2, n_1}^{(3)} = d \frac{n_1}{n} b_n. \quad (19)$$

If we interchange the roles of n_1 and n_2 in equation (19) and add the original and the transformed equations, we obtain equation (16). If, instead, we subtract both equations, we obtain

$$d[C_{n_1, n_2}^{(1)} - C_{n_2, n_1}^{(1)}] + (d-2)[C_{n_1, n_2}^{(2)} - C_{n_2, n_1}^{(2)}] - 2^{d-1}[C_{n_1, n_2}^{(3)} - C_{n_2, n_1}^{(3)}] = d \frac{n_1 - n_2}{n} b_n. \quad (20)$$

Thus, enforcement of equation (19) is equivalent to enforcement of equation (20). The property (14) guarantees that condition (20) is fulfilled by the coefficients in equations (8)–(10).

The most stringent conditions appear in the limits $\alpha \rightarrow 0$ and $\alpha \rightarrow \infty$. In that case, equation (7) yields

$$B_{n_1, n_2}^*(\alpha) = \begin{cases} v_d^{n-1} [C_{n_1, n_2}^{(3)} + C_{n_2, n_1}^{(1)}] & (\alpha \rightarrow 0), \\ v_d^{n-1} \alpha^d [C_{n_1, n_2}^{(1)} + C_{n_2, n_1}^{(3)}] & (\alpha \rightarrow \infty). \end{cases} \quad (21)$$

On the other hand, the *exact* result is [33, 34, 37]

$$B_{n_1, n_2}^*(\alpha) = \begin{cases} v_d^{n-1} \frac{n_2}{n} b_n & (\alpha \rightarrow 0), \\ v_d^{n-1} \alpha^d \frac{n_1}{n} b_n & (\alpha \rightarrow \infty). \end{cases} \quad (22)$$

The above condition means that, in the limit of infinite size asymmetry, the smaller spheres contribute to the total pressure as if they were a one-component system in a free volume equal to the total volume minus the volume occupied by the larger spheres. Our approximations (7)–(10) give the correct forms for the asymptotic behaviour of B_{n_1, n_2}^* , but not the correct coefficients (except for $n_2 = 1$ in the limit $\alpha \rightarrow 0$ and for $n_1 = 1$ in the limit $\alpha \rightarrow \infty$, apart from the trivial cases $n_1 = 0$, n and $n_2 = 0$, n). In fact, in our approximation the virial coefficient B_n depends parametrically on b_n only, and not on the previous coefficients b_{n_1} , $n_1 \leq n$, as is needed in equation (22). This is a consequence of the form of our approximation, in which the compressibility factor of the mixture at a given packing fraction η is expressed in terms of the compressibility factor of the monodisperse system at the same packing fraction.

Another consistency condition is [34]

$$\left. \frac{\partial B_{n-1, 1}^*}{\partial \alpha} \right|_{\alpha=0} = v_d^{n-1} d \frac{n-1}{n}. \quad (23)$$

This comes from the exact value of the derivative of the excess free energy with respect to molecular size in the

Table 1. Reduced virial coefficients b_n for the one-component case.

n	$d = 2^a$	$d = 3^a$	$d = 4^b$	$d = 5^b$
2	2	4	8	16
3	3.128 017 75	10	32.405 759 4	106
4	43.257 854 46	18.364 77	77.745 179 7	311.183 41
5	5.336 897	28.224 5	145.9	843.4
6	6.362 6	39.739	252.0	988
7	7.351	53.539		
8	8.338	70.78		

^a Reference [6].

^b References [7, 29, 30].

Table 2. Ratio R_n , as given by equation (25).

n	$d = 2$	$d = 3$	$d = 4$	$d = 5$
3	1.032	1	0.944	0.883
4	1.014	1.018	1.072	1.148
5	0.999	1.001	1.078	1.452
6	0.991	1.007	1.132	0.736
7	0.989	1.023		
8	0.992	1.047		

limit of infinite size asymmetry [38]. In general, this condition is not verified by our approximation either. We consider condition (22) to be more important than (23) because it is not restricted to $n_2 = 1$ (or $n_1 = 1$) and also because it refers to the leading term in the limit of infinite size asymmetry, while condition (23) refers to the subleading term.

Table 1 gives the known values of the coefficients b_n for $2 \leq d \leq 5$. From them, equations (7)–(11) can be used to estimate the coefficients B_{n_1, n_2}^* for any value of α in these dimensions. We will come back to this point later on. The values of table 1 can also be used to check the degree to which equation (22) is violated by approximations (7)–(10). The less favourable case corresponds to $n_1 = 1$ in the limit $\alpha \rightarrow 0$ (or, equivalently, $n_2 = 1$ in the limit $\alpha \rightarrow \infty$). Let us then define

$$R_n \equiv \frac{C_{1, n-1}^{(3)} + C_{n-1, 1}^{(1)}}{[(n-1)/n]b_{n-1}}. \tag{24}$$

According to equations (8) and (10), we have

$$R_n = \frac{(2^{2-d} + n - 3)b_n + 2^{d-1} - 1}{(n-1)b_{n-1}}. \tag{25}$$

Table 2 shows the values of R_n that can be obtained from the known virial coefficients. In the cases $d = 2$ and $d = 3$ the known values of ratio R_n differ from 1 less than 5%. In fact, by assuming $R_n \simeq 1$, equation (25) can be used to estimate b_9 and b_{10} . This gives $b_9 \simeq 9.39$

($d = 2$), $b_9 \simeq 86.7$ ($d = 3$), $b_{10} \simeq 10.44$ ($d = 2$) and $b_{10} \simeq 103.6$ ($d = 3$). Estimates based on Padé approximants are [6] $b_9 \simeq 9.37$ ($d = 2$), $b_9 \simeq 93.1$ ($d = 3$), $b_{10} \simeq 10.55$ ($d = 2$) and $b_{10} \simeq 123.2$ ($d = 3$). On the other hand, the deviations of R_n from 1 become more important as the dimensionality increases, and are already relatively large for $d = 5$. Thus, at least for those high dimensionalities, it appears to be convenient to modify prescription (7) to satisfy requirement (22). This is the subject of the next section, where we will also discuss in more detail how good the estimates of B_{n_1, n_2}^* , as obtained after using equations (7)–(11) with the values of the coefficients b_n given in table 1, are for any value of α and for $2 \leq d \leq 5$.

3. A new proposal for the equation of state of a binary mixture

In order to account for the conditions imposed by equation (22) without greatly sacrificing the simplicity of our original recipe, let us now explore the possibility of keeping the structure of equation (7), but with expressions for the coefficients different from those in equations (8)–(10). Requirement (22) implies that

$$C_{n_1, n_2}^{(3)} + C_{n_2, n_1}^{(1)} = \frac{n_2}{n} b_{n_2}. \tag{26}$$

In addition, condition (17) yields equation (16). Note that equation (13) is more restrictive than equation (16). Since we want our modified expressions to remain as close as possible to the original ones, we will take equation (13) as a second condition. From equations (26) and (13) we have

$$C_{n_1, n_2}^{(1)} = (2^{d-1} - 1)^{-1} \left[\frac{n_1}{n} (2^{d-1} b_{n_1} - b_n) + C_{n_2, n_1}^{(2)} \right], \tag{27}$$

$$C_{n_1, n_2}^{(3)} = (2^{d-1} - 1)^{-1} \left[\frac{n_2}{n} (b_n - b_{n_2}) - C_{n_1, n_2}^{(2)} \right]. \tag{28}$$

We need a third condition to close the problem. Since $C_{n_1, n_2}^{(2)}$ does not enter into equation (21) and, in agreement with our philosophy of departing from the original formulation as little as possible, one option is to keep

equation (9); however, the resulting approximation is consistent with condition (15) but does not satisfy requirement (19). If we enforce the fulfilment of equation (19) (or, equivalently, of equation (20)), then $C_{n_1, n_2}^{(2)}$ must have the following form

$$C_{n_1, n_2}^{(2)} = D_{n_1, n_2} - \frac{n_1 b_n - b_{n_1}}{n 2^{2-d} - 1}, \quad (29)$$

where D_{n_1, n_2} must be symmetric, but otherwise remains so far unknown. To close the problem, we impose the more restrictive property (14). This leads to

$$D_{n_1, n_2} = \frac{1}{n[2 + 2^{d-1}(d-3)]} \left[(2^{d-1} - 1)(2^{d-1} - db_n) \frac{n_1 n_2}{n-1} + \frac{2^{d-1} - d}{1 - 2^{2-d}} (nb_n - n_1 b_{n_1} - n_2 b_{n_2}) \right]. \quad (30)$$

Equations (27)–(30) close the modified version of our approximation.

It must be noted that equations (29) and (30) are meaningless if $d = 2$. This is related to the fact that if $d = 2$ it is impossible to enforce conditions (17), (18) and (22) simultaneously on a polynomial of second degree for B_{n_1, n_2}^* , as the number of conditions exceeds the number of unknowns. As a matter of fact, equations (27) and (28) are enough to determine B_{n_1, n_2}^* uniquely when $d = 2$, irrespective of the value of $C_{n_1, n_2}^{(2)}$. The result is

$$B_{n_1, n_2}^* = v_2^{n-1} \left[\frac{n_2}{n} b_{n_2} + \left(b_n - \frac{n_1}{n} b_{n_1} - \frac{n_2}{n} b_{n_2} \right) \alpha + \frac{n_1}{n} b_{n_1} \alpha^2 \right]. \quad (31)$$

This was the form proposed by Wheatley [33] by imposing conditions (17) and (22). However, condition (18) is not verified unless $n_1(b_n - b_{n_1}) = n_2(b_n - b_{n_2})$, which is true only if $b_n = n$, i.e. if one introduces scaled particle theory [39]. For the sake of comparison, the form that stems from our original approximation, equations (7)–(10), is (for $d = 2$)

$$B_{n_1, n_2}^* = v_2^{n-1} \frac{n_1 n_2}{n(n-1)} \left[\frac{n_2 - 1}{n_1} b_n + 1 + 2(b_n - 1)\alpha + \left(\frac{n_1 - 1}{n_2} b_n + 1 \right) \alpha^2 \right]. \quad (32)$$

In summary, the modified expressions for the virial coefficients are given by equation (31) for $d = 2$ and by equations (7) and (27)–(30) for $d \geq 3$. We are now in a position to compare the theoretical predictions we have provided in this and the previous section with the available Monte Carlo data for the virial coefficients. We note that the coefficients B_{n_1, n_2} corresponding to $n \leq 5$ have been evaluated for $d = 2$ [11, 15], $d = 3$

[12–14, 16], $d = 4$ [19] and $d = 5$ [19]. Further, the coefficients corresponding to $n = 6$ for $d = 2$ are known [18]. Because of its special physical interest and for reasons that will become apparent later, the case of hard spheres ($d = 3$) will be addressed separately in §4.

We begin our assessment of our estimates of B_{n_1, n_2} with the binary mixture of hard discs. This implies using equation (32) for the original recipe or using equation (31) in the modified version, which coincides with Wheatley’s proposal [33]. In figures 1–4 we compare the results of taking these two routes with those of [10, 11, 15, 18]. As seen in the figures, the theoretical prescriptions do a very good job of the whole range of α , the modified version (31) being almost perfect.

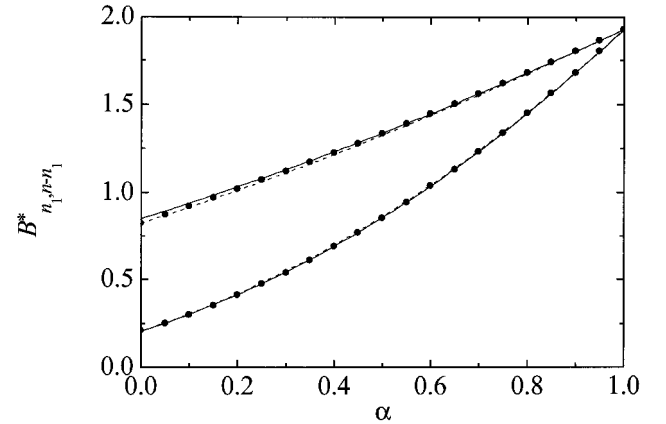


Figure 1. Reduced composition-independent virial coefficients $B_{n_1, n-1}^*$ as functions of the size ratio α for $d = 2$, $n = 3$, and, from top to bottom, $n_1 = 1$ and 2. The circles are exact results [10], the solid line is the theoretical prediction of equation (32) and the dashed line is the theoretical prediction of equation (31).

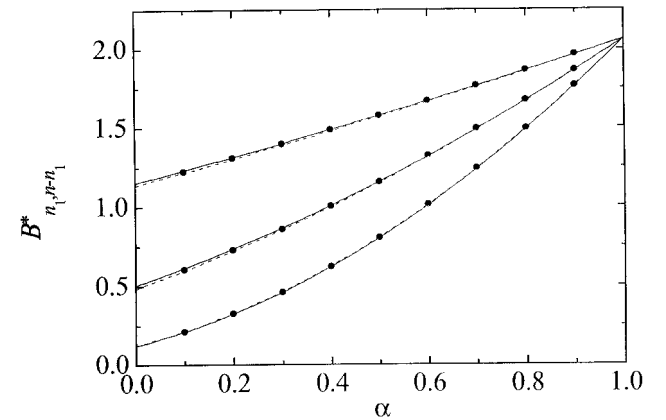


Figure 2. Reduced composition-independent virial coefficients $B_{n_1, n-1}^*$ as functions of the size ratio α for $d = 2$, $n = 4$, and, from top to bottom, $n_1 = 1, 2$ and 3. The circles are exact Monte Carlo results [11], the solid line is the theoretical prediction of equation (32) and the dashed line is the theoretical prediction of equation (31).

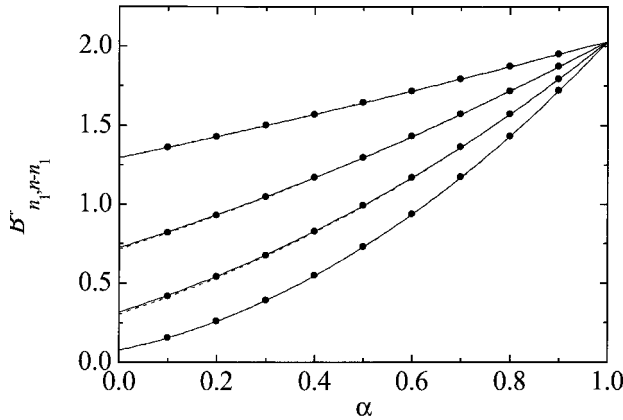


Figure 3. Reduced composition-independent virial coefficients $B_{n_1, n-n_1}^*$ as functions of the size ratio α for $d=2$, $n=5$, and, from top to bottom, $n_1 = 1, 2, 3$ and 4 . The circles are Monte Carlo results [15], the solid line is the theoretical prediction of equation (32) and the dashed line is the theoretical prediction of equation (31).

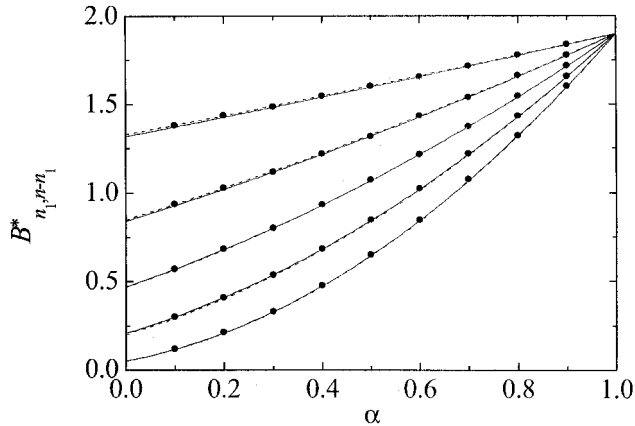


Figure 4. Reduced composition-independent virial coefficients $B_{n_1, n-n_1}^*$ as functions of the size ratio α for $d=2$, $n=6$, and, from top to bottom $n_1 = 1, 2, 3, 4$ and 5 . The circles are Monte Carlo results [18], the solid line is the theoretical prediction of equation (32) and the dashed line is the theoretical prediction of equation (31).

In the case of hard hyperspheres with $d=4$ and $d=5$, figures 5–10 illustrate the performance of equation (7) together with equations (8)–(11) and of equations (7) and (27)–(30) with respect to the ‘exact’ data of [19]. In these dimensionalities, it is clear that although the modified version of the estimates for the virial coefficients continues to exhibit a very good performance, the use of equations (7)–(11) presents limitations for $n=4$ and especially for $n=5$. Nevertheless, the EOS for the binary mixture derived from equation (2) (which yields the original estimates of the coefficients B_{n_1, n_2}), once the proper $Z_s(\eta)$ is used with both $d=4$ and $d=5$, turns out to be very accurate [36].

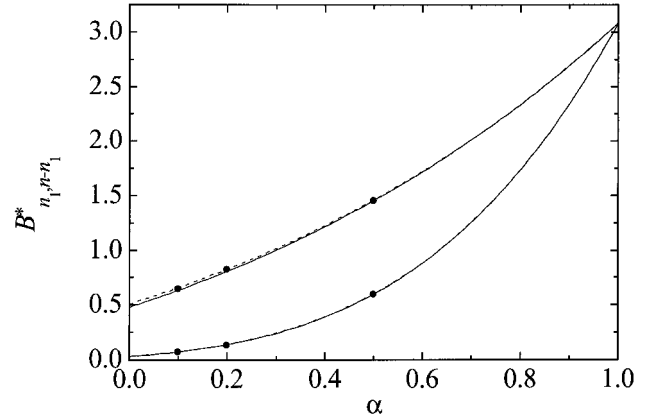


Figure 5. Reduced composition-independent virial coefficients $B_{n_1, n-n_1}^*$ as functions of the size ratio α for $d=4$, $n=3$, and, from top to bottom, $n_1 = 1$ and 2 . The circles are Monte Carlo results [19], the solid line is the theoretical prediction of equations (7)–(10) and the dashed line is the theoretical prediction given by equations (7) and (27)–(30).

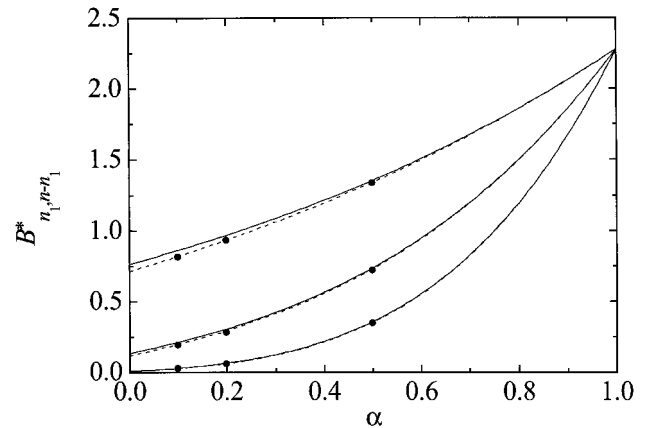


Figure 6. Reduced composition-independent virial coefficients $B_{n_1, n-n_1}^*$ as functions of the size ratio α for $d=4$, $n=4$, and, from top to bottom, $n_1 = 1, 2$ and 3 . The circles are Monte Carlo results [19], the solid line is the theoretical prediction of equations (7)–(10) and the dashed line is the theoretical prediction given by equations (7) and (27)–(30).

Once we have analysed the behaviour of the virial coefficients, the important question that now arises is, which is the EOS consistent with the modified virial coefficients? For $d=2$, from equation (31) one obtains [37]

$$Z_m(\eta) = \frac{x_1}{1-\eta_2} Z_s \left(\frac{\eta_1}{1-\eta_2} \right) \frac{\sigma_2 - \sigma_1}{\sigma_2} + \frac{x_2}{1-\eta_1} Z_s \left(\frac{\eta_2}{1-\eta_1} \right) \frac{\sigma_1 - \sigma_2}{\sigma_1} + Z_s(\eta) \frac{\langle \sigma^2 \rangle}{\sigma_1 \sigma_2}. \quad (33)$$

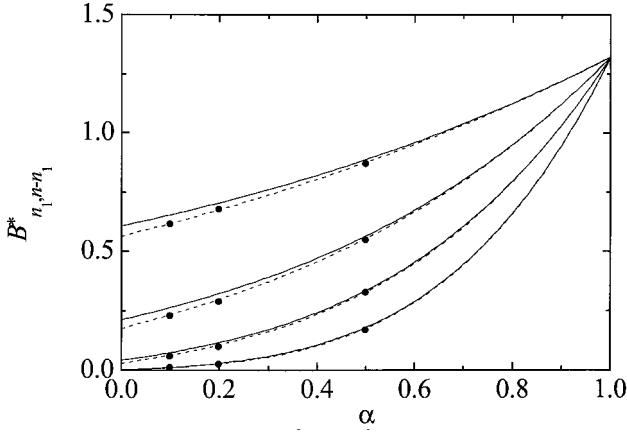


Figure 7. Reduced composition-independent virial coefficients $B_{n_1, n-n_1}^*$ as functions of the size ratio α for $d = 4$, $n = 5$, and, from top to bottom, $n_1 = 1, 2, 3$ and 4 . The circles are Monte Carlo results [19], the solid line is the theoretical prediction of equations (7)–(10) and the dashed line is the theoretical prediction given by equations (7) and (27)–(30).

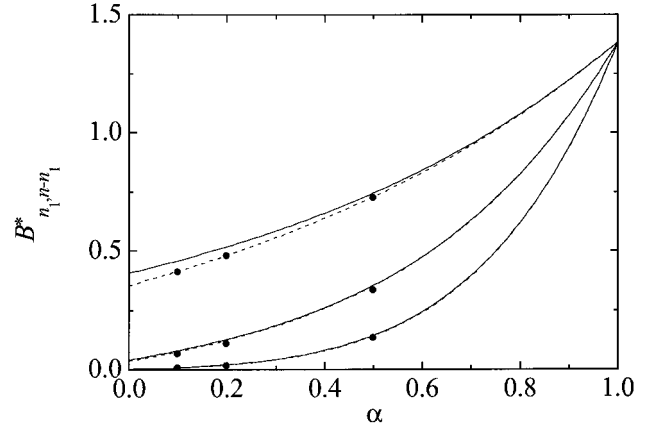


Figure 9. Reduced composition-independent virial coefficients $B_{n_1, n-n_1}^*$ as functions of the size ratio α for $d = 5$, $n = 4$, and, from top to bottom, $n_1 = 1, 2$, and 3 . The circles are Monte Carlo results [19], the solid line is the theoretical prediction of equations (7)–(10) and the dashed line is the theoretical prediction given by equations (7) and (27)–(30).

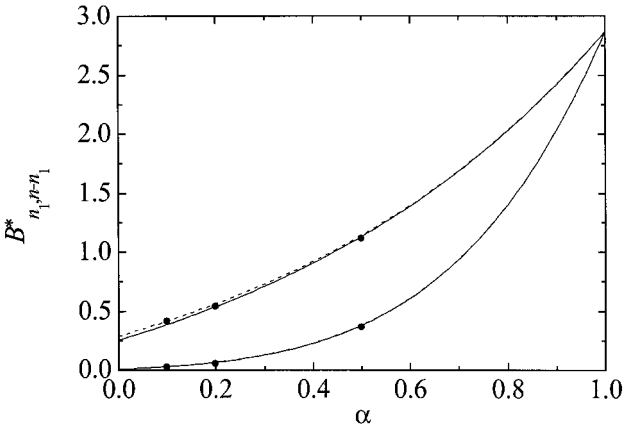


Figure 8. Reduced composition-independent virial coefficients $B_{n_1, n-n_1}^*$ as functions of the size ratio α for $d = 5$, $n = 3$, and, from top to bottom, $n_1 = 1$ and 2 . The circles are Monte Carlo results [19], the solid line is the theoretical prediction of equations (7)–(10) and the dashed line is the theoretical prediction given by equations (7) and (27)–(30).

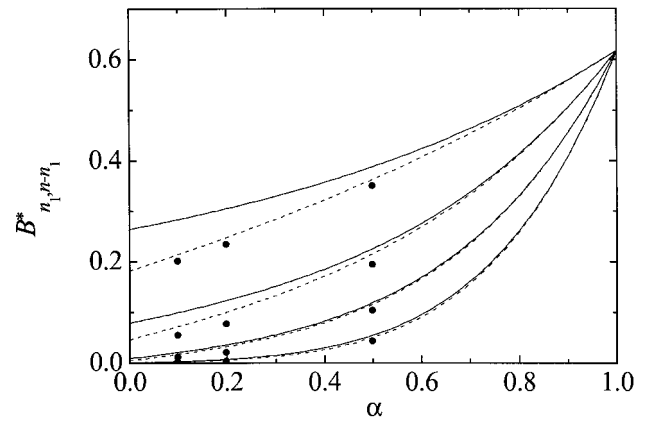


Figure 10. Reduced composition-independent virial coefficients $B_{n_1, n-n_1}^*$ as functions of the size ratio α for $d = 5$, $n = 5$, and, from top to bottom, $n_1 = 1, 2, 3$ and 4 . The circles are Monte Carlo results [19], the solid line is the theoretical prediction of equations (7)–(10) and the dashed line is the theoretical prediction given by equations (7) and (27)–(30).

The EOS consistent with equations (27)–(30) can also be explicitly obtained for $d \geq 3$ by carrying out the resummation of the corresponding virial series. The result is (see appendix B for details)

$$\begin{aligned}
 Z_m(\eta) = & 1 + \frac{K}{\langle \sigma^d \rangle} [Z_s(\eta) - 1] + \frac{K_0}{\langle \sigma^d \rangle} x_1 x_2 \frac{\eta}{1 - \eta} \\
 & + \frac{K_1}{\sigma_2^d} x_1 \left[\frac{1}{1 - \eta_2} Z_s \left(\frac{\eta_1}{1 - \eta_2} \right) - 1 \right] \\
 & + \frac{K_2}{\sigma_1^d} x_2^2 \left[\frac{1}{1 - \eta_1} Z_s \left(\frac{\eta_2}{1 - \eta_1} \right) - 1 \right], \quad (34)
 \end{aligned}$$

where K , K_0 , K_1 and K_2 are independent of the density and are given by

$$\begin{aligned}
 K = & x_1^2 \sigma_1^d \left(1 - \frac{K_1}{\sigma_2^d} \right) + x_2^2 \sigma_2^d \left(\frac{1 - K_2}{\sigma_1^d} \right) \\
 & + 2x_1 x_2 \left(\sigma_{12}^d - \frac{K_1 + K_2 + K_0}{2^d} \right), \quad (35)
 \end{aligned}$$

$$\begin{aligned}
 K_0 = & \frac{1}{2^{2-d} + d - 3} \\
 & \times [\sigma_1^d + \sigma_2^d + (2^{d-1} - 1) \sigma_1 \sigma_2 (\sigma_1^{d-2} + \sigma_2^{d-2}) - 2^d \sigma_{12}^d], \quad (36)
 \end{aligned}$$

$$K_1 = \frac{1}{(2^d - 4)(2^{2-d} + d - 3)\sigma_{12}} \times \{ \sigma_{12}^d [2^d(d-2)\sigma_1 + 8(1 - 2^{d-1} + d2^{d-3})\sigma_2] - (2^{d-1} - 2)\sigma_1\sigma_2(\sigma_1^{d-1} + \sigma_2^{d-1}) - (d-2)(2^{d-1} - 1)\sigma_1^2\sigma_2^{d-1} - (2^{d-1} - d)\sigma_1^{d-1}\sigma_2^2 - (d-2)\sigma_1^{d+1} - [d-4-2^{d-1}(d-3)]\sigma_2^{d+1} \}, \quad (37)$$

$$K_2 = \frac{1}{(2^d - 4)(2^{2-d} + d - 3)\sigma_{12}} \times \{ \sigma_{12}^d [2^d(d-2)\sigma_2 - 8(1 - 2^{d-1} + d2^{d-3})\sigma_1] - (2^{d-1} - 2)\sigma_1\sigma_2(\sigma_1^{d-1} + \sigma_2^{d-1}) - (d-2)(2^{d-1} - 1)\sigma_2^2\sigma_1^{d-1} - (2^{d-1} - d)\sigma_2^{d-1}\sigma_1^2 - (d-2)\sigma_2^{d+1} - [d-4-2^{d-1}(d-3)]\sigma_1^{d+1} \}. \quad (38)$$

Here, $\sigma_{12} \equiv (\sigma_1 + \sigma_2)/2$. Note that equation (33) for hard discs is included in the structure of equation (34), except that then equations (35)–(38) cannot be applied, and instead we have $K_0 = 0$, $K_1 = \sigma_2(\sigma_2 - \sigma_1)$, $K_2 = \sigma_1(\sigma_1 - \sigma_2)$ and $K = \langle \sigma^2 \rangle (1 - x_1 K_1/\sigma_2^2 - x_2 K_2/\sigma_1^2)$.

Equation (34) complies with the exact results given in equation (22). Clearly it is more complicated than the original recipe, equation (2), and should in principle be useful in particular for mixtures involving components of disparate sizes. In contrast to equation (2), proposal (34) expresses $Z_m(\eta)$ in terms not only of $Z_s(\eta)$ but also involves $Z_s(\eta_1/(1-\eta_2))$ and $Z_s(\eta_2/(1-\eta_1))$.

We note that if $d = 3$, it follows from equations (35)–(38) that $K_0 = 0$, $K_1 = \sigma_2(\sigma_1 - \sigma_2)^2$, $K_2 = \sigma_1(\sigma_1 - \sigma_2)^2$ and $K = \langle \sigma^3 \rangle (1 - x_1 K_1/\sigma_2^3 - x_2 K_2/\sigma_1^3)$. Consequently, equation (34) for hard spheres becomes

$$Z_m(\eta) = \frac{x_1}{1-\eta^2} Z_s\left(\frac{\eta_1}{1-\eta_2}\right) \frac{(\sigma_1 - \sigma_2)^2}{\sigma_2^2} + \frac{x_2}{1-\eta_1} Z_s\left(\frac{\eta_2}{1-\eta_1}\right) \frac{(\sigma_1 - \sigma_2)^2}{\sigma_1^2} + Z_s(\eta) \frac{2\langle \sigma^2 \rangle \sigma_1 \sigma_2 - \langle \sigma^4 \rangle}{\sigma_1^2 \sigma_2^2}. \quad (39)$$

It is interesting to note that equations (33) and (39) can be written in the common form

$$Z_m(\eta) = Z_s(\eta) + x_1 \left[\frac{1}{1-\eta_2} Z_s\left(\frac{\eta_1}{1-\eta_2}\right) - Z_s(\eta) \right] \times \left(\frac{\sigma_2 - \sigma_1}{\sigma_2} \right)^{d-1} + x_2 \left[\frac{1}{1-\eta_1} Z_s\left(\frac{\eta_2}{1-\eta_1}\right) - Z_s(\eta) \right] \times \left(\frac{\sigma_1 - \sigma_2}{\sigma_1} \right)^{d-1}. \quad (40)$$

Equation (40) reduces to equation (33) if $d = 2$ and to equation (39) if $d = 3$. In addition, it becomes exact for $d = 1$, i.e. $Z_s(\eta) = Z_m(\eta) = (1 - \eta)^{-1}$. It seems then very tempting to assume equation (40) for arbitrary d . With such an assumption, after using equations (B 3), (B 4), (B 8) and (B 9), we simply obtain for the composition-independent virial coefficients:

$$B_{n_1, n_2}^* = v_d^{n-1} \left[b_n \frac{n_1 \alpha^d + n_2}{n} + (b_{n_1} - b_n) \frac{n_1}{n} \alpha (\alpha - 1)^{d-1} + (b_{n_2} - b_n) \frac{n_2}{n} (1 - \alpha)^{d-1} \right]. \quad (41)$$

Of course, this includes the cases $d = 2$ [cf. equation (31)] and $d = 3$ [cf. equation (47)]. However, equation (41) differs from prescriptions (27)–(30) if $d \geq 4$. Although equation (41) is consistent with conditions (17) and (18) (for $d \geq 3$) and (22), it does not reproduce the exact second virial coefficient $B_{1,1}^*(\alpha) = v_d(1 + \alpha)^d/2$ (except, of course, for $d \leq 3$). In fact, we have checked that the performance of equations (40) and (41) is very poor for $d \geq 4$, and they will not be considered further here.

4. Equation of state of binary hard sphere mixtures

Up to here, although occasionally we have mentioned explicit features of hard discs and hard spheres, the developments presented in the previous sections apply for general dimensionality d . Given their intrinsic importance, in this section we focus on the results for the EOS in 3 dimensions. In order to set the framework of our discussion, we shall first recall two other EOSs in the literature which share with ours the idea of obtaining $Z_m(\eta)$ from knowledge of $Z_s(\eta)$.

The first is due to Hamad [40] who, in 1994 [41], derived a consistency condition involving the derivatives of the contact values of the radial distribution functions g_{ij} with respect to σ_k [42]. Imposing this condition, he proposed the following equation of state for hard sphere mixtures:

$$Z_m^H(\eta) = Z_s(\eta) + \frac{3\eta}{(1-\eta)^2} \left[\frac{\langle \sigma^2 \rangle^3}{\langle \sigma^3 \rangle^2} \eta + \frac{\langle \sigma \rangle \langle \sigma^2 \rangle}{\langle \sigma^3 \rangle} (1-\eta) - 1 \right], \quad (42)$$

where we have used the label H to refer to Hamad's proposal. It must be noted that equation (42) was not written explicitly in [40], where the results are expressed in a rather more involved form. The second EOS for binary mixtures of hard spheres that we want to consider was proposed more recently by Barrio and Solana [43] (label BS). It reads

$$Z_m^{\text{BS}}(\eta) = 1 + \frac{1}{4}(1 + \beta\eta) \left(1 + 3 \frac{\langle \sigma \rangle \langle \sigma^2 \rangle}{\langle \sigma^3 \rangle} \right) [Z_s(\eta) - 1], \quad (43)$$

where β is adjusted as to reproduce the exact third virial coefficient [9], namely

$$B_{3,0}^* = v_3^2 10 \alpha^3, \quad B_{2,1}^* = v_3^2 \left(\frac{4}{3} + 2\alpha + 5\alpha^2 + \frac{8}{3}\alpha^3 \right), \\ B_{1,2}^* = v_3^2 \left(\frac{8}{3} + 5\alpha + 2\alpha^2 + \frac{1}{3}\alpha^3 \right), \quad B_{0,3}^* = v_3^2 10. \quad (44)$$

More explicitly, in our notation β is written as

$$\beta = \frac{B_3}{v_3^2 \langle \sigma^3 \rangle^2 (1 + 3 \langle \sigma \rangle \langle \sigma^2 \rangle / \langle \sigma^3 \rangle)} - \frac{10}{4}. \quad (45)$$

We concentrate first on the composition-independent virial coefficients. Our original recipe, equations (7)–(10), gives for $d = 3$:

$$B_{n_1, n_2}^{\text{SYH}} = v_3^{n-1} \frac{n_1 n_2}{2n(n-1)(n-2)} \\ \times \left\{ 2(n_1 + 3n_2 - 4) + \frac{n_2 - 1}{n_1} (n_1 + 2n_2 - 4) b_n \right. \\ + [2(n_1 - 5n_2 + 4) + (n_1 + 4n_2 - 5) b_n] \alpha \\ + [2(n_2 - 5n_1 + 4) + (n_2 + 4n_1 - 5) b_n] \alpha^2 \\ \left. + \left[2(n_2 + 3n_1 - 4) + \frac{n_1 - 1}{n_2} (n_2 + 2n_1 - 4) b_n \right] \alpha^3 \right\}, \quad (46)$$

where we have incorporated the label SYH to distinguish it from the other results. On the other hand, in the 3-dimensional case equations (27)–(30) yield

$$B_{n_1, n_2}^{\text{W}} = v_3^{n-1} \left[\frac{n_2}{n} b_{n_2} + \left(\frac{2n_2 - n_1}{n} b_n + \frac{n_1}{n} b_{n_1} - 2 \frac{n_2}{n} b_{n_2} \right) \alpha \right. \\ \left. + \left(\frac{2n_1 - n_2}{n} b_n + \frac{n_2}{n} b_{n_2} - 2 \frac{n_1}{n} b_{n_1} \right) \alpha^2 + \frac{n_1}{n} b_{n_1} \alpha^3 \right], \quad (47)$$

which coincides with the form proposed by Wheatley [34] and so the label in this case is W. The virial coefficients associated with equations (42) and (43) are also readily derived. In the former case, first it is easy to obtain

$$B_n^{\text{H}} = v_3^{n-1} \langle \sigma^3 \rangle^{n-1} \left[b_n - \frac{3}{2} n(n-1) + 3(n-1) \frac{\langle \sigma \rangle \langle \sigma^2 \rangle}{\langle \sigma^3 \rangle} \right. \\ \left. + \frac{3}{2} (n-1)(n-2) \frac{\langle \sigma^2 \rangle^3}{\langle \sigma^3 \rangle^2} \right]. \quad (48)$$

Now, by making $m = 0$ and $m = 1$ in equation (A 2) and $m = 1$ in equation (A 1), and inserting the results into equation (48), we obtain the composition-independent coefficients arising from Hamad's proposal:

$$B_{n_1, n_2}^{\text{H}} = v_3^{n-1} \left\{ \frac{n_2}{n} \left[b_n - \frac{3}{2} n_1(n-1+n_2) \right] + \frac{3n_1 n_2}{2n} (3n_2-1) \alpha \right. \\ \left. + \frac{3n_1 n_2}{2n} (3n_1-1) \alpha^2 \right. \\ \left. + \frac{n_1}{n} \left[b_n - \frac{3}{2} n_2(n-1+n_1) \right] \alpha^3 \right\}. \quad (49)$$

As far as equation (43) is concerned, one may readily derive (for $n \geq 3$)

$$B_n^{\text{BS}} = \frac{v_3^{n-1}}{4} (b_n + \beta b_{n-1}) \langle \sigma^3 \rangle^{n-1} \left(1 + 3 \frac{\langle \sigma \rangle \langle \sigma^2 \rangle}{\langle \sigma^3 \rangle} \right) \\ = \frac{v_3^{n-1}}{4} \left(b_n - \frac{10}{4} b_{n-1} \right) \langle \sigma^3 \rangle^{n-1} \left(1 + 3 \frac{\langle \sigma \rangle \langle \sigma^2 \rangle}{\langle \sigma^3 \rangle} \right) \\ + \frac{v_3^{n-3}}{4} b_{n-1} B_3 \langle \sigma^3 \rangle^{n-3}. \quad (50)$$

Now, after some algebra also involving the substitution of the results obtained by taking $m = 0$ and $m = 1$ in equation (A 2) into equation (50), the composition-independent virial coefficients for the Barrio–Solana EOS turn out to be given by

$$B_{n_1, n_2}^{\text{BS}} = v_3^{n-1} \frac{b_n}{4n(n-1)} [n_2(3n_2+n-4) + 3n_1 n_2 \alpha \\ + 3n_1 n_2 \alpha^2 + n_1(3n_1+n-4) \alpha^3] - v_3^{n-1} \frac{3b_{n-1} n_1 n_2}{8n(n-1)(n-2)} \\ \times [n + 2n_2 - 4 + (n - 6n_2 + 4) \alpha \\ + (n - 6n_1 + 4) \alpha^2 + (n + 2n_1 - 4) \alpha^3]. \quad (51)$$

These four approximations for B_{n_1, n_2}^* satisfy requirements (17) and (18). Condition (22) is satisfied only by the W approximation, while condition (23) is satisfied only by the H approximation. By construction, the BS approximation, equation (51), reproduces the exact third virial coefficients of equation (44). It is interesting to point out that approximations (46), (47) and (49) also yield the exact value of the third virial coefficients.

In order to assess the accuracy of the previous approximate expressions for B_{n_1, n_2}^* with $n \geq 4$, we will take the case $n_1 = 3$, $n_2 = 1$ as a benchmark for comparison, since the coefficient $B_{3,1}^*$ has been obtained *exactly* for the interval $0 \leq \alpha \leq 2/\sqrt{3} - 1 \simeq 0.1547$ [17]. The exact result is

$$B_{3,1}^* = \frac{v_3^3}{4} (1 + 9\alpha + 36\alpha^2 + 21\alpha^3 + \frac{27}{2}\alpha^4 + \frac{27}{10}\alpha^5 - \frac{108}{5}\alpha^6 - \frac{648}{35}\alpha^7 - \frac{81}{14}\alpha^8 - \frac{9}{14}\alpha^9). \quad (52)$$

Setting $n_1 = 3$ and $n_2 = 1$ in equations (46), (47), (49) and (51), respectively, yields

$$B_{3,1}^{\text{SYH}} = \frac{v_3^3}{4} \left[1 + \left(\frac{b_4}{2} + 1 \right) \alpha + (2b_4 - 5)\alpha^2 + 3 \left(\frac{b_4}{2} + 1 \right) \alpha^3 \right], \quad (53)$$

$$B_{3,1}^{\text{W}} = \frac{v_3^3}{4} [1 + (28 - b_4)\alpha + (5b_4 - 59)\alpha^2 + 30\alpha^3], \quad (54)$$

$$B_{3,1}^{\text{H}} = \frac{v_3^3}{4} [b_4 - 18 + 9\alpha + 36\alpha^2 + 3(b_4 - 9)\alpha^3], \quad (55)$$

and

$$B_{3,1}^{\text{BS}} = \frac{v_3^3}{16} [b_4 - 15 + (3b_4 - 15)\alpha + (3b_4 + 75)\alpha^2 + (9b_4 - 45)\alpha^3]. \quad (56)$$

Note that equations (53) and (54) would coincide if b_4 were equal to 18, as happens with the CS equation of state. However, they differ if we take the exact value $b_4 = 18.36477$. The maximum deviation of equation (54) from the exact result (equation (52)) is about 1.8% (for $\alpha \simeq 0.08$), while that of equation (53) is about 3.7% (for $\alpha \simeq 0.09$). Also, if b_4 were equal to 19, equation (55) would coincide with equation (54), while using the exact value for b_4 implies that $\lim_{\alpha \rightarrow 0} B_{3,1}^{\text{H}} = 0.091v_3^3$ instead of the exact value $\lim_{\alpha \rightarrow 0} B_{3,1}^* = \frac{1}{4}v_3^3$, which, however, is satisfied by approximations (53) and (54). Comparison between Hamad's approximation (55) and the exact result (52) for $\alpha \leq 2/\sqrt{3} - 1$ shows that the relative error of equation (55) monotonically decreases from about 64% at $\alpha = 0$ to about 18% at $\alpha = 2/\sqrt{3} - 1$. Finally, according to equation (56) with the exact value of b_4 , $\lim_{\alpha \rightarrow 0} B_{3,1}^{\text{BS}} = 0.210v_3^3$, while in the interval $\alpha \leq 2/\sqrt{3} - 1$ the relative error of equation (56) monotonically decreases from about 16% at $\alpha = 0$ to about 1.7% at $\alpha = 2/\sqrt{3} - 1$. This relative error is always larger than that of equations (53) and (54), but smaller than that of equation (55).

Apart from the exact result for $B_{3,1}^*$, as pointed out above, numerical values of the coefficients B_{n_1, n_2}^* corresponding to $n \leq 5$ are also available for hard spheres [12–14, 16]. In figures 11 and 12 we display a comparison between the theoretical estimates we have just discussed for the virial coefficients and the numerical results. It is clear that the estimates $B_{n_1, n_2}^{\text{SYH}}$, B_{n_1, n_2}^{W} and B_{n_1, n_2}^{BS} for $n = 4$ and $n = 5$ are remarkably close to one

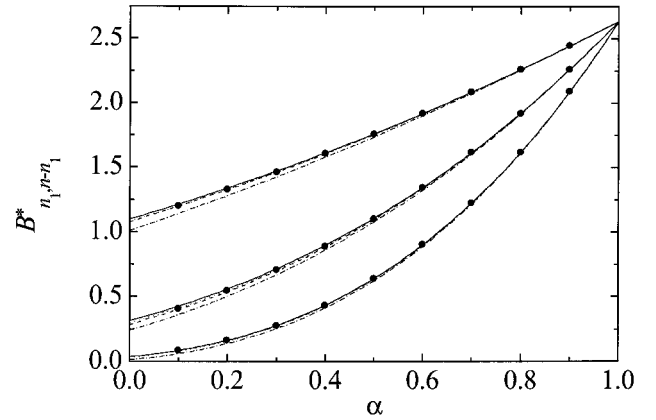


Figure 11. Reduced composition-independent virial coefficients B_{n_1, n_2}^* as functions of the size ratio α for $d = 3$, $n = 4$, and, from top to bottom, $n_1 = 1, 2$ and 3 . The circles are Monte Carlo results [13], the solid line is the theoretical prediction of equation (46), the dashed line is the theoretical prediction of equation (47), the dash-dotted line is the theoretical prediction of equation (49) and the dotted line is the theoretical prediction of equation (51).

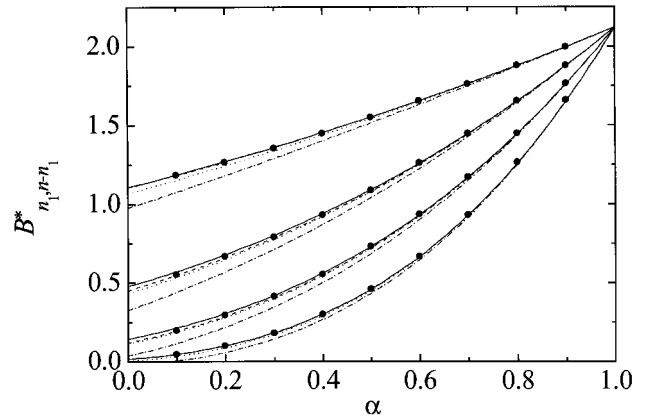


Figure 12. Reduced composition-independent virial coefficients B_{n_1, n_2}^* as functions of the size ratio α for $d = 3$, $n = 5$, and, from top to bottom, $n_1 = 1, 2, 3$ and 4 . The circles are Monte Carlo results [14, 16], the solid line is the theoretical prediction of equation (46), the dashed line is the theoretical prediction of equation (47), the dash-dotted line is the theoretical prediction of equation (49) and the dotted line is the theoretical prediction of equation (51).

another and to the exact results, except perhaps in the case of $B_{1,4}^{\text{BS}}$. On the other hand, the prediction of B_{n_1, n_2}^{H} is much poorer.

Once we have briefly discussed the performance of the various approximate expressions for the composition-independent virial coefficients, we may next contemplate how well the approximate EOS for a binary mixture of hard spheres performs with respect to the simulation data. To address this issue, we first need to specify

what $Z_s(\eta)$ is. Two choices will be made here. On the one hand, since perhaps the most popular and widely known EOS for a single-component fluid of hard spheres is the CS EOS, we will also use it here. On the other hand, a more accurate EOS for the same system is obtained if a rescaled Padé approximation taking into account the known virial coefficients is used [24]. We should point out that the approximation used in [24] is

somewhat different from the one used here, since apparently the number of significant figures in the value of the virial coefficients is not the same in the two instances. We have checked that the present approximation yields practically identical results. In tables 3 and 4 we present a comparison of the results obtained using the various approximate EOSs for the mixture with these two choices of $Z_s(\eta)$, two different mole fractions and a

Table 3. Comparison of the compressibility factor from several equations of state with simulation values (Z_{simul}) for binary additive mixtures of hard spheres ($d = 3$) with size ratio $\alpha = 0.3$. The fourth to seventh columns give the deviations from Z_{simul} of the values of the compressibility factor as obtained from equations of state (2), (39), (42) and (43), respectively. In these equations of state, the Carnahan–Starling compressibility factor for the one-component fluid [25] has been used. For the sake of comparison, also the results arising from the Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) equation of state [44] are included.

x_1	η	Z_{simul}^a	Eq. (2) ^b	Eq. (39) ^c	Eq. (42) ^d	Eq. (43) ^e	BMCSL
0.0625	0.3	2.790	−0.001	−0.009	−0.061	−0.016	−0.014
	0.35	3.473	0.006	−0.011	−0.112	−0.024	−0.020
	0.4	4.410	0.013	−0.019	−0.210	−0.043	−0.035
	0.45	5.722	0.027	−0.033	−0.385	−0.076	−0.063
	0.49	7.158	0.065	−0.036	−0.603	−0.102	−0.081
0.75	0.3	3.554	−0.005	−0.006	−0.024	−0.010	−0.008
	0.35	4.601	−0.012	−0.014	−0.048	−0.021	−0.018
	0.4	6.045	−0.010	−0.014	−0.079	−0.027	−0.021
	0.45	8.097	−0.002	−0.011	−0.129	−0.033	−0.022
	0.49	10.415	−0.004	−0.021	−0.210	−0.056	−0.037

^a Reference [45].

^b Reference [32].

^c This work.

^d Reference [40].

^e Reference [43].

Table 4. Comparison of the compressibility factor from several equations of state with simulation values (Z_{simul}) for binary additive mixtures of hard spheres ($d = 3$) with size ratio $\alpha = 0.3$. The fourth to seventh columns give the deviations from Z_{simul} of the values of the compressibility factor as obtained from the equations of state (2), (39), (42) and (43), respectively. In these equations of state, a rescaled Padé approximant compressibility factor for the one-component fluid [24] (see text) has been used.

x_1	η	Z_{simul}^a	Eq. (2) ^b	Eq. (39) ^c	Eq. (42) ^d	Eq. (43) ^e
0.0625	0.3	2.790	0.004	−0.005	−0.050	−0.010
	0.35	3.473	0.014	−0.004	−0.095	−0.014
	0.4	4.410	0.025	−0.008	−0.186	−0.029
	0.45	5.722	0.043	−0.018	−0.353	−0.058
	0.49	7.158	0.084	−0.015	−0.564	−0.081
0.75	0.3	3.554	0.003	0.002	−0.013	−0.001
	0.35	4.601	0.001	−0.001	−0.032	−0.007
	0.4	6.045	0.010	0.006	−0.055	−0.007
	0.45	8.097	0.025	0.016	−0.096	−0.006
	0.49	10.415	0.028	0.012	−0.171	−0.023

^a Reference [45].

^b Reference [32].

^c This work.

^d Reference [40].

^e Reference [43].

diameter ratio $\alpha = 0.3$. In table 3, the values corresponding to the widely used Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) EOS [44] have also been included. One immediately notes that, as already stated in the literature [24, 32, 35], the EOS given in equation (2) using the CS EOS for the single-component system provides a very accurate account of the simulation data, better than any of the other EOS for mixtures considered, including that of equation (39). If instead of the CS EOS the rescaled Padé approximation is taken for $Z_s(\eta)$, then it is equation (39) which gives, in general, the best results, although the original recipe (2) and the BS EOS (43) are not too far behind, the latter being especially accurate for $x_1 = 0.75$. It should be noted that, irrespective of the choice for $Z_s(\eta)$, both $Z_m^H(\eta)$ and $Z_m^{BS}(\eta)$ for this size ratio and these packing fractions always underestimate the simulation results, a comment that applies also to the BMCSL EOS.

5. Conclusion

We have further assessed the merits and limitations of a simple recipe recently introduced [32] to derive the compressibility factor of a multicomponent mixture of d -dimensional hard spheres. We have now considered the case of binary mixtures, and looked in particular at the composition-independent virial coefficients. A comparison with the available exact and simulation results confirmed the usefulness of our approach except perhaps when the mixture involves components of very disparate sizes (especially for high dimensionalities). Guided by the conditions that the virial coefficients must comply with certain limits, a slight modification of the form of the original coefficients was made, trying to sacrifice simplicity as little as possible while at the same time improving the accuracy of their numerical predictions. It is fair to state that the (modified) composition-independent virial coefficients are in excellent agreement with the reported values for all dimensions and all size ratios.

Due to its particular relevance, the case of the binary mixture of hard spheres ($d = 3$) was analysed in some detail, both in connection with the virial coefficients and through the consideration of different EOSs for this system that exist in the literature. As for the virial coefficients, the trends pointed out above about the reliability of the original and modified prescriptions hold also for $d = 3$. A comparison with the simulation results for the compressibility factor of these mixtures given in tables 3 and 4 indicates the superiority of the original recipe for the EOS, provided that one uses the CS EOS for $Z_s(\eta)$. On the other hand, if the more accurate rescaled Padé approximation for $Z_s(\eta)$ is used, it is the new EOS (equation (39), i.e. the one obtained after resumming

the virial series with the modified coefficients) which gives the best performance, although only slightly better than $Z_m(\eta)$ as given by equation (2) with $d = 3$. Both equations are also of comparable accuracy to presumably one of the best EOSs available presently for hard sphere mixtures, namely the rescaled Padé approximant for mixtures introduced by Malijevský and Veverka [24]. This equation of state rests on a different philosophy, however, in the sense that it makes use of the known virial coefficients of the mixture rather than the $Z_s(\eta)$, as in our approach and those of Hamad [40] and Barrio and Solana [43].

In conclusion, we wish to add that both the original proposal of the EOS of a binary mixture of d -dimensional hard spheres, equation (2), and the modified version, equation (34), provide a simple yet accurate EOS, at least with respect to the composition-independent virial coefficients and in comparison with (relatively scarce) simulation data. Further confirmation of their usefulness depends on new simulations, which we hope will be encouraged by the results presented in this paper.

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Appendix A

Derivation of equations (7)–(10)

In order to identify the composition-independent coefficients B_{n_1, n_2} from equation (5), we need to expand the moments $\langle \sigma^p \rangle$. After some algebra, we obtain

$$\begin{aligned} & \langle \sigma^d \rangle^{n-3} \langle \sigma^{d-m} \rangle \langle \sigma^{m+1} \rangle \langle \sigma^{d-1} \rangle \\ &= \sigma_1^{d(n-1)} \sum_{n_1=0}^n \alpha^{d(n-n_1-1)} \frac{(n-3)!}{n_1!(n-n_1)!} x_1^{n_1} x_2^{n-n_1} \\ & \quad \times [n_1(n_1-1)(n_1-2)\alpha^d + n_1(n_1-1)(n-n_1)\alpha^{d-1} \\ & \quad + n_1(n_1-1)(n-n_1)\alpha^{d-m} + n_1(n-n_1)(n-n_1-1)\alpha^{d-m-1} \\ & \quad + n_1(n_1-1)(n-n_1)\alpha^{m+1} + n_1(n-n_1)(n-n_1-1)\alpha^m \\ & \quad + n_1(n-n_1)(n-n_1-1)\alpha \\ & \quad + (n-n_1)(n-n_1-1)(n-n_1-2)], \end{aligned} \tag{A1}$$

and

$$\begin{aligned}
 & \langle \sigma^d \rangle^{n-2} \langle \sigma^{d-m} \rangle \langle \sigma^m \rangle \\
 &= \sigma_1^{d(n-1)} \sum_{n_1=0}^n \alpha^{d(n-n_1-1)} \frac{(n-2)!}{n_1!(n-n_1)!} x_1^{n_1} x_2^{n-n_1} \\
 & \quad \times [n_1(n_1-1)\alpha^d + n_1(n-n_1)\alpha^{d-m} \\
 & \quad + n_1(n-n_1)\alpha^m + (n-n_1)(n-n_1-1)], \quad (\text{A } 2)
 \end{aligned}$$

where $\alpha \equiv \sigma_2/\sigma_1$. Now we use the identities

$$\sum_{m=0}^d \frac{d!}{m!(d-m)!} \alpha^m = (1+\alpha)^d, \quad (\text{A } 3)$$

$$\sum_{m=0}^d \frac{(d-1)!}{m!(d-m)!} (d-m)\alpha^m = (1+\alpha)^{d-1}, \quad (\text{A } 4)$$

to obtain

$$\begin{aligned}
 & \sum_{m=0}^d \frac{(d-1)!}{m!(d-m)!} (d-m) \langle \sigma^d \rangle^{n-3} \langle \sigma^{d-m} \rangle \langle \sigma^{m+1} \rangle \langle \sigma^{d-1} \rangle \\
 &= \sigma_1^{d(n-1)} \sum_{n_1=0}^n \alpha^{d(n-n_1-1)} \frac{(n-3)!}{n_1!(n-n_1)!} \\
 & \quad \times x_1^{n_1} x_2^{n-n_1} [n_1(n_1-1)(n_1-2)2^{d-1}\alpha^d \\
 & \quad + n_1(n_1-1)(n-n_1)2^{d-1}\alpha^{d-1} \\
 & \quad + 2n_1(n_1-1)(n-n_1)\alpha(1+\alpha)^{d-1} \\
 & \quad + 2n_1(n-n_1)(n-n_1-1)(1+\alpha)^{d-1} \\
 & \quad + n_1(n-n_1)(n-n_1-1)2^{d-1}\alpha \\
 & \quad + (n-n_1)(n-n_1-1)(n-n_1-2)2^{d-1}], \quad (\text{A } 5)
 \end{aligned}$$

and

$$\begin{aligned}
 & \sum_{m=0}^d \frac{d!}{m!(d-m)!} \langle \sigma^d \rangle^{n-2} \langle \sigma^{d-m} \rangle \langle \sigma^m \rangle \\
 &= \sigma_1^{d(n-1)} \sum_{n_1=0}^n \alpha^{d(n-n_1-1)} \frac{(n-2)!}{n_1!(n-n_1)!} x_1^{n_1} x_2^{n-n_1} \\
 & \quad \times [n_1(n_1-1)2^d\alpha^d + 2n_1(n-n_1)(1+\alpha)^d \\
 & \quad + (n-n_1)(n-n_1-1)2^d]. \quad (\text{A } 6)
 \end{aligned}$$

From here finally we obtain equations (7)–(10).

Appendix B

Derivation of equations (34)–(38)

Let us rewrite equation (7) as

$$\begin{aligned}
 B_{n_1, n_2} &= v_d^{n-1} [C_{n_1, n_2}^{(1)} \sigma_1^{d(n_1-1)} \sigma_2^{dn_2} + C_{n_1, n_2}^{(2)} \sigma_1^{d(n_1-1)+1} \sigma_2^{dn_2-1} \\
 & \quad + C_{n_1, n_2}^{(3)} 2^{d-1} \sigma_{12}^{d-1} \sigma_1^{d(n_1-1)+1} \sigma_2^{d(n_2-1)} + 1 \leftrightarrow 2], \quad (\text{B } 1)
 \end{aligned}$$

where $\sigma_{12} \equiv (\sigma_1 + \sigma_2)/2$ and the notation $1 \leftrightarrow 2$ indicates that a contribution similar to the three summands appearing in the brackets in which the roles of (n_1, n_2) and of (σ_1, σ_2) are interchanged (i.e. $n_1 \rightarrow n_2$, $\sigma_1 \rightarrow \sigma_2$ and vice versa) should be added. The compressibility factor of the mixture is then given by

$$\begin{aligned}
 Z_m(\eta) - 1 &= \sum_{n=2}^{\infty} \rho^{n-1} \sum_{n_1=0}^n B_{n_1, n_2} \frac{n!}{n_1! n_2!} x_1^{n_1} x_2^{n_2} \\
 &= \sum_{n=2}^{\infty} (v_d \rho)^{n-1} \sum_{n_1=0}^n \frac{n!}{n_1! n_2!} x_1^{n_1} x_2^{n_2} \\
 & \quad \times [C_{n_1, n_2}^{(1)} \sigma_1^{d(n_1-1)} \sigma_2^{dn_2} + C_{n_1, n_2}^{(2)} \sigma_1^{d(n_1-1)+1} \sigma_2^{dn_2-1} \\
 & \quad + C_{n_1, n_2}^{(3)} 2^{d-1} \sigma_{12}^{d-1} \sigma_1^{d(n_1-1)+1} \sigma_2^{d(n_2-1)}] \\
 & \quad + 1 \leftrightarrow 2. \quad (\text{B } 2)
 \end{aligned}$$

Now we insert equations (27)–(30) and sum over n_1 and n . To do that, we use the identities

$$\begin{aligned}
 x_1 [Z_s(\eta) - 1] &= \sum_{n=2}^{\infty} (v_d \rho)^{n-1} \sum_{n_1=0}^n \frac{n!}{n_1! n_2!} x_1^{n_1} x_2^{n_2} b_n \\
 & \quad \times \frac{n_1}{n} \sigma_1^{d(n_1-1)} \sigma_2^{dn_2}, \quad (\text{B } 3)
 \end{aligned}$$

$$\begin{aligned}
 x_2 [Z_s(\eta) - 1] &= \sum_{n=2}^{\infty} (v_d \rho)^{n-1} \sum_{n_1=0}^n \frac{n!}{n_1! n_2!} x_1^{n_1} x_2^{n_2} b_n \\
 & \quad \times \frac{n_2}{n} \sigma_1^{dn_1} \sigma_2^{d(n_2-1)}, \quad (\text{B } 4)
 \end{aligned}$$

$$\begin{aligned}
 \langle \sigma^d \rangle [Z_s(\eta) - 1] &= \sum_{n=2}^{\infty} (v_d \rho)^{n-1} \sum_{n_1=0}^n \frac{n!}{n_1! n_2!} \\
 & \quad \times x_1^{n_1} x_2^{n_2} b_n \sigma_1^{dn_1} \sigma_2^{dn_2}, \quad (\text{B } 5)
 \end{aligned}$$

$$\begin{aligned}
 x_1 x_2 \frac{Z_s(\eta) - 1}{\langle \sigma^d \rangle} &= \sum_{n=2}^{\infty} (v_d \rho)^{n-1} \sum_{n_1=0}^n \frac{n!}{n_1! n_2!} x_1^{n_1} x_2^{n_2} b_n \\
 & \quad \times \frac{n_1 n_2}{n(n-1)} \sigma_1^{d(n_1-1)} \sigma_2^{d(n_2-1)}, \quad (\text{B } 6)
 \end{aligned}$$

$$\begin{aligned}
 x_1 x_2 \frac{\eta}{(1-\eta) \langle \sigma^d \rangle} &= \sum_{n=2}^{\infty} (v_d \rho)^{n-1} \sum_{n_1=0}^n \frac{n!}{n_1! n_2!} x_1^{n_1} x_2^{n_2} \\
 & \quad \times \frac{n_1 n_2}{n(n-1)} \sigma_1^{d(n_1-1)} \sigma_2^{d(n_2-1)}. \quad (\text{B } 7)
 \end{aligned}$$

In addition [37],

$$\frac{x_1}{1-\eta_2} Z_s \left(\frac{\eta_1}{1-\eta_2} \right) - x_1 = \sum_{n=2}^{\infty} (v_d \rho)^{n-1} \sum_{n_1=0}^n \frac{n!}{n_1! n_2!} x_1^{n_1} x_2^{n_2} b_{n_1} \frac{n_1}{n} \sigma_1^{d(n_1-1)} \sigma_2^{dn_2}, \quad (\text{B } 8)$$

$$\frac{x_2}{1-\eta_1} Z_s \left(\frac{\eta_2}{1-\eta_1} \right) - x_2 = \sum_{n=2}^{\infty} (v_d \rho)^{n-1} \sum_{n_1=0}^n \frac{n!}{n_1! n_2!} x_1^{n_1} x_2^{n_2} b_{n_2} \frac{n_2}{n} \sigma_1^{dn_1} \sigma_2^{d(n_2-1)}. \quad (\text{B } 9)$$

This allows one to obtain $Z_m(\eta)$ in terms of Z_s evaluated at η , $\eta_1/(1-\eta_2)$ and $\eta_2/(1-\eta_1)$. After some algebra, we arrive at equations (34)–(38).

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