

# Is it possible to infer the equation of state of a mixture of hard discs from that of the one-component system?

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Based on exact asymptotic properties of the composition-independent virial coefficients of a binary mixture of hard discs in the limits  $\alpha \equiv \sigma_2/\sigma_1 \rightarrow 0$ ,  $\alpha \rightarrow 1$  and  $\alpha \rightarrow \infty$ , R. J. Wheatley (1998, *Molec. Phys.*, **93**, 965) has recently proposed an approximate interpolation equation for these coefficients. In this note, the equation of state equivalent to this interpolation is obtained, expressing the compressibility factor of the mixture in terms of that of the pure system. An extension to an arbitrary number of components is also given. The equation of state derived here is compared with another one recently proposed by following a different route (Santos, A., Yuste, S. B., and López de Haro, M., 1999, *Molec. Phys.*, **96**, 1) and with Monte Carlo simulation results. It is shown that the latter equation is more accurate than the former one, at least for not too disparate mixtures ( $0.7 \leq \alpha < 1$ ).

In the last few years, the search and proposal of accurate equations of state for mixtures of hard discs or hard spheres has received renewed attention [1–4]. This has been stimulated in part by the recent (numerical) calculation of the fourth and fifth virial coefficients for these systems [5–8]. The aim of this note is to obtain an expression for the equation of state of a binary mixture of hard discs in terms of the equation of state of the pure system, by starting from an interpolation formula for the virial coefficients recently proposed by Wheatley [3, 7]. Moreover, this expression is extended to any number of components. The equation of state obtained here is compared with another one recently proposed [4] and with Monte Carlo simulation data [9].

An  $m$ -component system of hard discs is characterized by the total number density  $\rho = N/V$  ( $N$  being the total number of particles and  $V$  being the area), the set of molar fractions  $\{x_i\} = \{x_1, x_2, \dots, x_m\}$  and the set of diameters  $\{\sigma_i\} = \{\sigma_1, \sigma_2, \dots, \sigma_m\}$ . A quantity more useful than  $\rho$  as a measure of the density of the system is the area packing fraction  $\eta = \sum_{i=1}^m \eta_i$ , where  $\eta_i = (\pi/4)x_i\rho\sigma_i^2$  is the fraction of the total area occupied by the discs of species  $i$ . The equation of state of the system is given by the compressibility factor  $pV/Nk_B T \equiv Z^{(m)}(\eta; \{x_i\}, \{\sigma_i\})$ , where  $p$  is the pressure,  $k_B$  is the Boltzmann constant and  $T$  is the temperature. Apart from the packing fraction  $\eta$ , the compressibility factor depends on  $2(m-1)$  parameters:  $m-1$  independent molar fractions (since  $\sum_{i=1}^m x_i = 1$ ) and  $m-1$  independent diameter ratios (since  $Z^{(m)}$  is a dimensionless quantity). In the particular case of a binary mixture ( $m=2$ ), one has  $Z^{(2)}(\eta; x_1, \alpha)$ , where  $\alpha \equiv \sigma_2/\sigma_1$ . Most

of the exact knowledge of the equation of state comes from the virial coefficients  $B_n^{(m)}$ , which are the coefficients in the expansion of the compressibility factor in powers of density:

$$Z^{(m)}(\eta; \{x_i\}, \{\sigma_i\}) = \sum_{n=1}^{\infty} B_n^{(m)}(\{x_i\}, \{\sigma_i\})\rho^{n-1}. \quad (1)$$

For one-component systems,  $B_n^{(1)}(\sigma) = (\pi\sigma^2/4)^{n-1}b_n$ , where the  $b_n$  are pure numbers. In the case of binary mixtures, the virial coefficients  $B_n^{(2)}$  can be expanded in terms of composition-independent components:

$$B_n^{(2)}(x_1, \sigma_1, \sigma_2) = \sum_{n_1=0}^n \frac{n!}{n_1!(n-n_1)!} B_{n_1, n-n_1}(\sigma_1, \sigma_2) x_1^{n_1} x_2^{n-n_1}. \quad (2)$$

Obviously,  $B_{n,0}(\sigma_1, \sigma_2) = (\pi\sigma_1^2/4)^{n-1}b_n$  and  $B_{0,n}(\sigma_1, \sigma_2) = (\pi\sigma_2^2/4)^{n-1}b_n$ . Also, if  $\alpha \equiv \sigma_2/\sigma_1 = 1$ , we trivially have  $B_{n_1, n-n_1}(\sigma, \sigma) = (\pi\sigma^2/4)^{n-1}b_n$ . Much subtler conditions are derived in the limits  $\alpha \rightarrow 0$  and  $\alpha \rightarrow \infty$  by regarding the smaller discs as occupying a free area equal to the total area minus the area of the larger discs. Thus, one has [3]

$$\begin{aligned} B_{n_1, n_2}(\sigma_1, \alpha\sigma_1) &= \left(\frac{\pi\sigma_1^2}{4}\right)^{n-1} \alpha^{2(n_2-1)} \frac{n_2}{n} b_{n_2} \quad (\alpha \rightarrow 0), \\ &= \left(\frac{\pi\sigma_1^2}{4}\right)^{n-1} b_n \quad (\alpha = 1), \\ &= \left(\frac{\pi\sigma_1^2}{4}\right)^{n-1} \alpha^{2n_2} \frac{n_1}{n} b_{n_1} \quad (\alpha \rightarrow \infty), \end{aligned} \quad (3)$$

where  $n \equiv n_1 + n_2$  and  $1 \leq n_1 \leq n - 1$ . Wheatley [3] constructed fitting functions for the fourth and fifth virial coefficients by using the above exact properties and his numerical results [7] for  $\alpha = 0.1, 0.2, \dots, 0.9$ . Based on equation (3), he also proposed estimates for the sixth to eighth coefficients by means of the interpolation formula

$$B_{n_1, n_2}(\sigma_1, \alpha\sigma_1) = \left(\frac{\pi\sigma_1^2}{4}\right)^{n-1} \alpha^{2(n_2-1)} \left[ \frac{n_2}{n} b_{n_2} + \left(b_n - \frac{n_1}{n} b_{n_1} - \frac{n_2}{n} b_{n_2}\right) \alpha + \frac{n_1}{n} b_{n_1} \alpha^2 \right], \quad (4)$$

where the virial coefficients  $b_n$ ,  $n \leq 8$ , of the one-component fluid are known [10]. In addition, Wheatley [3] proposed the following rational function approximation for the equation of state,

$$Z^{(2)}(\eta; x_1, \alpha) = \frac{\sum_{n=0}^7 c_n(x_1, \alpha) \eta^n}{(\eta_0 - \eta)^2}, \quad (5)$$

where  $\eta_0 = 3^{1/2}\pi/6$  is the close-packing fraction of the pure substance and the eight coefficients  $c_n$  are chosen so that equation (5) reproduces the exact second and third virial coefficients, the fourth and fifth virial coefficients as given by his approximate fitting functions, and the sixth to eighth virial coefficients as given by equation (4).

What I propose here is a different application of equation (4). The first step consists of assuming that equation (4) gives reasonable estimates for *every* value of  $n$ . This assumption is supported by the fact that equation (4) is exact for  $n = 2$  and is remarkably accurate for  $n = 3, 4, 5$ . In the next step, the infinite series expansion (1) (with  $m = 2$ ) is resummed. As a result, the compressibility factor of the binary mixture is expressed in terms of that of the pure system as

$$Z^{(2)}(\eta; x_1, \alpha) = (1 - \alpha^{-1}) \frac{x_1}{1 - \eta_2} Z^{(1)}\left(\frac{\eta_1}{1 - \eta_2}\right) + (1 - \alpha) \frac{x_2}{1 - \eta_1} Z^{(1)}\left(\frac{\eta_2}{1 - \eta_1}\right) + \frac{x_1 + x_2 \alpha^2}{\alpha} Z^{(1)}(\eta). \quad (6)$$

Equation (6) expresses the pressure of the mixture as a linear combination of three terms: (i) the pressure that particles of species 1 would have if they behaved as a pure system in a free area equal to the total area minus the area occupied by the other species; (ii) the same, but for species 2; and (iii) the pressure associated with a pure substance occupying the same area fraction as the true mixture. In the limits  $\alpha \rightarrow 0$  or  $\alpha \rightarrow \infty$ , equation (6) becomes

$$Z^{(2)}(\eta; x_1, \alpha) \rightarrow x_1 Z^{(1)}(\eta) + [x_s/(1 - \eta)] Z^{(1)}(\eta_s/(1 - \eta)),$$

where the subscripts  $l$  and  $s$  refer to the larger and the smaller discs, respectively. This is precisely the starting point to derive (3). Let us check now that equation (6) leads to equation (4). First, note that

$$\begin{aligned} \frac{x_1}{1 - \eta_2} Z^{(1)}\left(\frac{\eta_1}{1 - \eta_2}\right) &= \frac{x_1}{1 - \eta_2} \sum_{n_1=1}^{\infty} b_{n_1} \left(\frac{\eta_1}{1 - \eta_2}\right)^{n_1-1} \\ &= x_1 \sum_{n_1=1}^{\infty} \sum_{n_2=0}^{\infty} \frac{(n_1 + n_2 - 1)!}{(n_1 - 1)! n_2!} b_{n_1} \eta_1^{n_1-1} \eta_2^{n_2} \\ &= \sum_{n=1}^{\infty} \left(\frac{\pi}{4}\rho\right)^{n-1} \sum_{n_1=1}^n \frac{(n-1)!}{(n_1-1)! n_2!} x_1^{n_1} x_2^{n_2} b_{n_1} \sigma_1^{2(n_1-1)} \sigma_2^{2n_2}, \end{aligned} \quad (7)$$

where, as before,  $n = n_1 + n_2$ . Analogously,

$$\begin{aligned} \frac{x_2}{1 - \eta_1} Z^{(1)}\left(\frac{\eta_2}{1 - \eta_1}\right) &= \sum_{n=1}^{\infty} \left(\frac{\pi}{4}\rho\right)^{n-1} \sum_{n_1=0}^{n-1} \frac{(n-1)!}{n_1! (n_2-1)!} x_1^{n_1} x_2^{n_2} b_{n_2} \sigma_1^{2n_1} \sigma_2^{2(n_2-1)}. \end{aligned} \quad (8)$$

Finally,

$$\begin{aligned} (x_1 \sigma_1^2 + x_2 \sigma_2^2) Z^{(1)}(\eta) &= \sum_{n=1}^{\infty} \left(\frac{\pi}{4}\rho\right)^{n-1} b_n (x_1 \sigma_1^2 + x_2 \sigma_2^2)^n \\ &= \sum_{n=1}^{\infty} \left(\frac{\pi}{4}\rho\right)^{n-1} b_n \sum_{n_1=0}^n \\ &\quad \times \frac{n!}{n_1! n_2!} x_1^{n_1} x_2^{n_2} \sigma_1^{2n_1} \sigma_2^{2n_2}. \end{aligned} \quad (9)$$

From equations (7)–(9) one can easily identify the composition-independent coefficients  $B_{n_1, n_2}$  associated with the equation of state (6) and confirm that they coincide with Wheatley's interpolation, equation (4). This proves the full equivalence of equations (4) and (6).

Since the exact equation of state of the pure system is not known, equation (6) actually defines a family of equations of state for the binary mixture. It is rewarding that if one assumes that the pure system is described by the Scaled Particle Theory (SPT), i.e.  $Z^{(1)}(\eta) = (1 - \eta)^{-2}$ , then equation (6) reduces to the SPT equation of state for a mixture [9], which for an arbitrary number of components reads

$$Z^{(m)}(\eta; \{x_i\}, \{\sigma_i\}) = \frac{1 - (1 - \langle \sigma \rangle^2 / \langle \sigma^2 \rangle) \eta}{(1 - \eta)^2}, \quad (10)$$

where  $\langle \sigma^\ell \rangle \equiv \sum_{i=1}^m x_i \sigma_i^\ell$ . A drawback of equation (6) is that it only applies to *binary* mixtures. On the other hand, using as a guide the requirement that it reduces again to equation (10) if  $Z^{(1)}(\eta) = (1 - \eta)^{-2}$ , I propose the following extension:

$$\begin{aligned} Z^{(m)}(\eta; \{x_i\}, \{\sigma_i\}) &= \sum_{i=1}^m \frac{\langle \sigma^2 \rangle - \langle \sigma \rangle \sigma_i}{\langle \sigma^2 \rangle - x_i \sigma_i^2} \frac{x_i}{1 + \eta_i - \eta} \\ &\times Z^{(1)}\left(\frac{\eta_i}{1 + \eta_i - \eta}\right) \\ &+ \sum_{i=1}^m x_i \sigma_i \frac{\langle \sigma \rangle - x_i \sigma_i}{\langle \sigma^2 \rangle - x_i \sigma_i^2} Z^{(1)}(\eta). \end{aligned} \quad (11)$$

The reader can easily check the consistency of equation (11) with equation (10). In the polydisperse limit, i.e.  $m \rightarrow \infty$  and  $x_i \rightarrow 0$  (which implies  $\eta_i \rightarrow 0$ ), equation (11) simplifies to

$$Z^{(m)}(\eta; \{x_i\}, \{\sigma_i\}) = \left(1 - \frac{\langle \sigma \rangle^2}{\langle \sigma^2 \rangle}\right) \frac{1}{1 - \eta} + \frac{\langle \sigma \rangle^2}{\langle \sigma^2 \rangle} Z^{(1)}(\eta). \quad (12)$$

It turns out that the equation of state (12) has been recently proposed for *finite*  $m$  (even  $m = 2$ ) by following a completely different approach [4]. Thus, we can see equation (12) as an alternative equation of state, independent of equations (6) or (11). Both equations of state (11) and (12) are consistent with equation (12); in addition, they tend to overlap as the number of components increases. The main advantage of equation (12) lies on its simplicity, clearly superior to that of equation (11). On the other hand, based on the analysis of the virial coefficients, one could in principle expect equation (12) to be less accurate than equation (11). For instance, in the binary case equation (12) yields

$$\begin{aligned} B_{n_1, n_2}(\sigma_1, \alpha \sigma_1) &= \left(\frac{\pi \sigma_1^2}{4}\right)^{n-1} \alpha^{2(n_2-1)} \frac{n_1 n_2}{n(n-1)} \\ &\times \left[ \frac{n_2 - 1}{n_1} b_n + 1 + 2(b_n - 1) \alpha \right. \\ &\left. + \left(\frac{n_1 - 1}{n_2} b_n + 1\right) \alpha^2 \right]. \end{aligned} \quad (13)$$

While equation (13) has the same structure as equation (4), it does not comply with the properties (3), except if (and only if)  $b_n = n$ , which corresponds to the SPT equation of state.

In order to test the reliability of equations (6) and (12) for a binary mixture, we will compare their predictions with Monte Carlo simulation data [9]. To do so, we need to assume an equation of state for the pure system. For illustration purposes, two choices will be made here. First, we take the simple equation proposed by Santos and co-workers [11],

$$Z^{(1)}(\eta) = \left(1 - 2\eta + \frac{2\eta_0 - 1}{\eta_0^2} \eta^2\right)^{-1}. \quad (14)$$

Although this equation is constructed under the only requirements of reproducing the second virial coefficient  $b_2 = 2$  and having a pole at the crystalline close-packing fraction  $\eta_0$ , it has a better agreement with simulations than some other more sophisticated equations. Second, we take the equation proposed by Henderson [12],

$$Z^{(1)}(\eta) = \frac{1 + (b_3 - 3)\eta^2}{(1 - \eta)^2} - c_H \frac{\eta^4}{(1 - \eta)^3}, \quad (15)$$

where  $b_3 = 16/3 - 4(3^{1/2})/\pi$  and the constant  $c_H = 0.043$  is fitted to optimize the agreement with simulations. In a recent work, Mulero *et al.* [13] have shown that equation (15) is perhaps the most accurate available equation of state for hard discs. Table 1 shows the values of the quantity  $p\sigma_1^2/k_B T$  for some dense binary mixtures, as obtained from Monte Carlo simulations [9] and from equations (5), (6) and (12), the two latter complemented by equations (14) and (15).

From the results of the table, it follows that the best agreement with the simulation data generally corresponds to equation (12), either in connection with equation (14) (typically for  $\eta > 0.55$ ) or in connection with equation (15) (typically for  $\eta \leq 0.55$ ). The second observation is that equation (5) usually performs better than equation (6). As a summary of table 1, the average absolute deviations from the simulation results are 0.08 for the equation of state (5), 0.12 for the combination of equations (6) and (14), 0.10 for equations (6) + (15), 0.05 for equations (12) + (14) and 0.06 for equations (12) + (15); the average relative deviations are 1.6%, 2.5%, 2.0%, 1.1% and 1.1%, respectively. It is also interesting to remark that the difference between the pressures given by equations (6) and (12) is practically independent of the choice of the one-component equation of state.

To sum up, in this note the equation of state equivalent to the interpolation equation (4) proposed by Wheatley [3, 7] for a binary mixture of hard discs has been obtained. This equation of state, cf. equation (6), expresses the compressibility factor of the mixture in terms of that of the pure system. An extension to an arbitrary number of components, equation (11), has also been proposed. This gives an affirmative answer

Table 1. Comparison of Monte Carlo simulation values [9] of the quantity  $p\sigma_1^2/k_B T$  with the predictions of several equations of state: equation (5) proposed by Wheatley [3], equation (6) derived in this paper, complemented by equations (14) and (15), and equation (12) proposed in [4], complemented by equations (14) and (15).

$\alpha$	$x_1$	$\eta$	Simul.	(5)	(6)+(14)	(6)+(15)	(12)+(4)	(12)+(15)
0.9	0.48	0.54	3.70	3.72	3.64	3.69	3.65	3.71
0.9	0.49	0.63	6.54	6.78	6.67	6.68	6.68	6.69
0.8	0.65	0.55	4.05	4.06	4.10	4.15	4.00	4.05
0.8	0.315	0.55	4.72	4.71	4.44	4.50	4.63	4.70
0.8	0.52	0.60	5.88	5.96	5.94	5.98	5.87	5.91
0.8	0.315	0.60	6.33	6.55	6.17	6.21	6.45	6.50
0.7	0.546	0.55	4.55	4.57	4.60	4.66	4.50	4.56
0.8	0.351	0.481	3.00	3.03	2.89	2.93	2.98	3.02
0.8	0.351	0.532	4.00	4.14	3.94	4.00	4.07	4.13
0.8	0.351	0.548	4.50	4.57	4.36	4.42	4.50	4.56
0.8	0.351	0.564	5.00	5.07	4.83	4.89	4.98	5.05
0.8	0.351	0.579	5.50	5.59	5.32	5.38	5.50	5.56

to the question posed in the title. In fact, this answer has already been considered in [4], where a general recipe for any dimensionality is given. In the special case of a two-dimensional system, the above recipe becomes equation (12). It is amazing that equation (12) has been 'rederived' here by taking in equation (11) the limit of a polydisperse mixture. Despite the fact that equation (12) is simpler than equation (6), comparison with simulation results [9] shows that it is also more accurate, at least for not very disparate binary mixtures ( $0.7 \leq \alpha < 1$ ). On the other hand, since equation (12) is not fully consistent with the numerical coefficients in the asymptotic properties (3), it might be that equation (6), or more generally equation (11), becomes preferable over equation (12) for disparate mixtures ( $\alpha \ll 1$ ). In order to explore this possibility, it is very important that more extensive simulations are carried out.

Finally, it is important to note that the extension of equations (5) or (6) to any dimensionality  $d$  is not straightforward. The corresponding asymptotic behaviours of the composition-independent coefficients are  $B_{n_1, n_2}(\sigma_1, \alpha\sigma_2) \sim (v_d\sigma_1^d)^{n-1} \alpha^{d(n_2-1)} (n_2/n) b_{n_2}$  and  $B_{n_1, n_2}(\sigma_1, \alpha\sigma_2) \sim (v_d\sigma_1^d)^{n-1} \alpha^{dn_2} (n_1/n) b_{n_1}$  when  $\alpha \rightarrow 0$  and  $\alpha \rightarrow \infty$ , respectively, where  $v_d$  is the volume of a sphere of unit diameter. This suggests to approximate  $B_{n_1, n_2}(\sigma_1, \alpha\sigma_2) \sigma_1^{-d(n-1)} \alpha^{-d(n_2-1)}$  by a polynomial in  $\alpha$  of degree  $d$ , but the number of coefficients exceeds in  $d-2$  the number of conditions. In fact, Wheatley *et al.* [8] have proposed such a polynomial interpolation for  $d=3$  and fixed the extra coefficient by a fit to the numerical values of the virial coefficients.

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