About the Usage of Scaling Parameters in the Scaled Particle Theory of Mixtures of Non-Additive Hard Spheres

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A new simple equation of state is derived for symmetric and asymmetric mixtures of non-additive hard spheres. The derivation of the equation of state is reminiscent of the scaled particle theory. However, this method uses two scaling parameters, which depend on the composition of the mixture. As a result, the equation of state presented here approaches in a natural way the limit of the one component fluid. This feature of the present theory stands in sharp contrast to common scaled particle theories for non-additive hard spheres, where the one component limit has an unphysical dependence on the non-additivity. The equation of state can be used for mixtures of particles that differ in size and has a second and a third virial coefficient which are exact up to first order in the non-additivity. The compressibility factors and the demixing densities predicted by the present equation of state are in fairly good agreement which available MC data.

Introduction

The scaled particle theory was one of the first theories which yielded a simple and accurate equation of state for the hard sphere fluid [1]. Later this equation of state, known as the compressibility equation, was also obtained from the Percus-Yevick closure of the Ornstein-Zernike equation [2]. A generalisation of the scaled particle theory to mixtures of spheres that are additive in the collision diameters ($\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ with $i, j = 1, 2$) was given by Lebowitz et al. [3].

The success of the scaled particle theory has inspired several workers to investigate whether this scheme can also applied to more complex fluids. One of those fluids is the mixture of non-additive hard spheres. In this mixture the particles interact via the following pair potential:

$$V_{jk}(r) = \begin{cases} 0 & \text{for} \quad r \geq R_j + R_k + \alpha(1-\delta_{jk}) \\ \infty & \text{for} \quad r < R_j + R_k + \alpha(1-\delta_{jk}) \end{cases}, \qquad (1)$$

where R_i is radius of a particle of component i, α is the non-additivity length and δ_{jk} is the Kronecker delta. The results for non-additive hard spheres as obtained by scaled particle theory are not completely satisfying. Recently Bearman and Mazo [4] have presented a version of the scaled particle theory for binary mixtures of non-additive hard spheres that reproduces fairly accurately the reported demixing densities for mixtures with positive non-additivities. However their theory, as well as a previous version of the scaled particle theory [5], has the disadvantage that it yields for the limit of the one component system an equation of state that depends on the non-additivity length [4]. This defect is possibly caused by the usage of a composition-independent scaling parameter.

Here an equation of state is derived for the binary non-additive hard sphere mixture using a scheme that is reminiscent of the scaled particle theory. Rather than using one scaling interaction parameter that is independent of the composition of the mixture, two composition dependent scaling lengths are used. These scaling lengths will be determined in such a manner that the equation of state yields good approximations for the second and third virial coefficients. The derivation presented here is restricted to mixtures with relatively small values of the non-additivity parameter $\Delta = \alpha/(R_1 + R_2)$. This is reasonable since most non-additivities in the collision diameters that are found experimentally in Ne+Xe mixtures [6], He+H_2 mixtures [7], water+gas mixtures [8] and alloys [9, 10] are within $-0.1 < \Delta < 0.1$. The equation of state presented here is simple for symmetric ($R_1 = R_2$) and asymmetric mixtures ($R_1 \neq R_2$).

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Theory

Equation (1) reduces to the pair potentials of a mixture of additive hard spheres when the non-additivity length $\alpha = 0$. For additive hard sphere mixtures very accurate, simple equations of state are known [11, 12]. From (1) it is evident that in certain limits the thermodynamic properties of the non-additive hard sphere mixture should approach the thermodynamic properties of an additive mixture. Therefore it is possible to formulate several boundary conditions that should be fulfilled by the chemical potentials of a mixture of non-additive hard spheres. The chemical potential of component j is given by

$$\mu_j = \mu_{j,\mathrm{id}} + W_j(R_j, R_k, \alpha)\,. \tag{2}$$

Here $\mu_{\mathrm{id}} = \ln[\varrho_i h^3/(2\pi m_i k_B T)^{3/2}]$ is the ideal gas part of the chemical potential. The nonideal configurational term $W_j(R_j, R_k, \alpha)$ is equal to the reversible amount of work that is required for inserting a particle of species j into the mixture [3]. In (2) and in what follows $j \neq k$.

The first boundary condition can be obtained in the limit that the mole fraction x_j of component j approaches zero. Then one has a mixture of many particles of component k with a radius R_k and only a few particles of component j which have a effective radius of $R_j + \alpha$. Therefore the configurational term $W_j^{\mathrm{na}}(R_j, R_k, \alpha)$ of the non-additive mixture should approach the configurational term $W_j^{\mathrm{add}}(R_j + \alpha;\, R_k)$ of an additive mixture of hard spheres with radii $R_j + \alpha$ and R_k. This boundary condition can be summarized as

(i) $\quad x_j \to 0 \;\Rightarrow\; W_j^{\mathrm{na}}(R_j, R_k, \alpha) = W_j^{\mathrm{add}}(R_j + \alpha, R_k)\,.$

Similarly one finds for the opposite composition range

(ii) $\quad x_j \to 1 \;\Rightarrow\; W_j^{\mathrm{na}}(r_j, R_k, \alpha) = W_j^{\mathrm{add}}(r_j, R_k + \alpha)\,.$

The third boundary condition is obtained when the limit $\alpha = 0$ is considered:

(iii) $\quad \alpha = 0 \;\Rightarrow\; W_j^{\mathrm{na}}(R_j, R_k, \alpha) = W_j^{\mathrm{add}}(R_j, R_k)\,.$

These boundary conditions should be fulfilled by an equation of state for mixtures of non-additive hard spheres. In addition, the resulting equation of state should yield good approximations for the second virial coefficient

$$B_2 = \frac{2\pi}{3}\,(x_j^2 R_{jj}^3 + x_k^2 R_{kk}^3 + 2 x_j x_k (R_{jk} + \alpha)^3) \tag{3a}$$

and the third virial coefficient $C_3 = \sum\limits_{lmn} x_l x_m x_n C_{lmn}$ with [12]

$$C_{sst} = C_{sts} = \frac{\pi^2}{54}\,(R_{ss}^6 + 32 R_{ss}^3 \sigma_{st}^3 - 18 R_{ss}^4 \sigma_{st}^2) \tag{3b}$$

with $R_{st} = R_s + R_t$ and $\sigma_{st} = R_{st} + \alpha(1 - \delta_{st})$. The expression for C_{sst} is only valid when $R_{ss} + 2\sigma_{st} \geq 2\max(R_{ss}, \sigma_{st})$. An expression for C_{sst} of the opposite case $R_{ss} + 2\sigma_{st} \leq 2\max(R_{ss}, \sigma_{st})$ can be found in [13]. However, this opposite case is not of interest here, since it corresponds to very large negative non-additivities.

One of the simplest expressions for $W_j^{\mathrm{na}}(R_j, R_k, \alpha)$ that fulfills the boundary conditions (i)–(iii) is given by

$$\begin{aligned} &W_j^{\mathrm{na}}(R_j, R_k, \alpha) \\ &\quad = x_j W_j^{\mathrm{add}}(R_j, R_k + b_k \alpha) + x_k W_j^{\mathrm{add}}(R_j + b_j \alpha, R_k)\,. \end{aligned} \tag{4}$$

The function b_j depends only on the mole fraction and the radii R_j and R_k. For boundary conditions (i) and (ii) it is essential that b_j approaches 1 when x_k approaches 1. The explicit expression for b_j is chosen in such a way that the resulting equation of state yields good approximations for the second and third virial coefficients B_2 and C_3.

The actual expression for W_j^{add} can be obtained from an equation of state for mixtures of additive hard spheres, using the thermodynamic relationships $p = N^{-1}\varrho^2(\partial A/\partial\varrho)_{T,x,N}$ and $\mu_j = V^{-1}(\partial A/\partial\varrho_j)_{T,V,N_{i \neq j}}$. Here p, N, V, A, represent the pressure, the total number of articles, the volume of the system and the Helmholtz free energy, respectively. The number density of component j is $\varrho_j = x_j N/V = x_j \varrho$. Here I will consider

$$\begin{aligned} \beta W_j^{\mathrm{add}}(R, R_k) = &- \ln(1 - \xi_3) + \frac{6\xi_2}{(1 - \xi_3)} R \\ &+ \left[\frac{12\xi_1}{(1 - \xi_3)} + \frac{18\xi_2^2}{(1 - \xi_3)^2}\right] R^2 + \tfrac{4}{3}\pi\beta p R^3 \\ &- \theta\left(6\,\frac{\xi_2^2}{\xi_3}\left[\frac{3\xi_3 - 2}{(1 - \xi_3)^2} - \frac{2\ln(1 - \xi_3)}{\xi_3}\right] R^2\right. \\ &\left.+ \frac{8\xi_2^3}{\xi_3^2}\left[\frac{4\xi_3^2 - 5\xi_3 + 2}{(1 - \xi_3)^3} + \frac{2\ln(1 - \xi_3)}{\xi_3}\right] R^3\right) \end{aligned} \tag{5}$$

with

$$\xi_n = (\pi/6) \sum_{i = j,k} \varrho_i (2R_i)^n\,. \tag{6}$$

Equation (5) generates the compressibility equation of state for additive mixtures for $\theta = 0$, the Carnahan-

Starling equation for $\theta=1$, and the virial equation for $\theta=3$ [3, 11, 12]. More refined theories have been constructed in which θ is a function of the density [11]. However these theories will not be considered here. It should be noted that the compressibility-, the Carnahan-Starling- and the virial equations of state for additive hard spheres yield exact second and third virial coefficients.

Combination of (5), (4) and (2) yields the chemical potential. Then the equation of state can be obtained by integrating the Gibbs-Duhem equation

$$\left(\frac{\mathrm{d}p}{\mathrm{d}\varrho}\right)=\sum_i \varrho_i\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}\varrho_j}\right). \tag{7}$$

Using (5) one finds on the right hand side of the Gibbs-Duhem equation that the density is always multiplied by a function of the mole fraction. This indicates that (7) is an exact differential equation [14]. Therefore the result of the integration of (7) is independent of the integration path [14]. Equation (7) can be integrated analytically along a constant composition path. Then the resulting compressibility factor $Z=p/k_\mathrm{B}T\varrho$ for mixtures of non-additive hard spheres is found to be

$$\begin{aligned}Z=\sum_i \frac{x_i}{\xi_0}\Bigg[L_i \ln\left(\frac{1-\xi_{i3}}{1-\Gamma}\right)+M_i\frac{1}{1-\xi_{i3}}\\ -4.5\,K_i\frac{\xi_{i2}^3}{\xi_{i3}(1-\xi_{i3})^2}-\theta\,\frac{\xi_{i2}^3\,\xi_{i3}}{(1-\xi_{i3})^3}\Bigg]\end{aligned} \tag{8}$$

with

$$\xi_{jn}=\frac{\pi}{6}\sum_i \varrho_i(2(R_i+b_i\,\alpha(1-\delta_{ij})))^n\,, \tag{9}$$

$$\begin{aligned}\Gamma &=\sum_l x_l\,\xi_{l3}\,,\\ K_i &=1/(\Gamma-\xi_{i3})\,,\\ L_i &=K_i\,\xi_0+6K_i^2\,\xi_{i1}\,\xi_{i2}+9K_i^3\,\xi_{i2}^3\,,\\ M_i &=-6K_i\,\xi_{i1}\,\xi_{i2}+4.5K_i^2\,\xi_{i2}^3(\Gamma-3\xi_{i2}^3)/\xi_{i3}\,.\end{aligned}$$

For $\alpha=0$, (8) reduces to the equation of state for mixtures of additive hard spheres that corresponds to the chosen value of θ.

A special type of non-additive mixtures that is often studied, is the equimolar symmetric mixture: $R_j=R_k$ and $x_j=x_k=0.5$. In this symmetric case $\xi_{jn}=\xi_{kn}$ is valid for all values of n. For this special case it can be shown by series expansion that (8) reduces to

$$\begin{aligned}&Z(x_j=0.5,\ R_j=R_k)\\ &=\frac{1}{1-\xi_{j3}}+\frac{3\,\xi_{j1}\,\xi_{j2}}{\xi_0(1-\xi_{j3})^2}+\frac{3\,\xi_{j2}^3-\theta\,\xi_{j2}^3\,\xi_{j3}}{\xi_0(1-\xi_{j3})^3}\,.\end{aligned} \tag{10}$$

Equation (10) has the form of the equation of state for mixtures of additive hard spheres when the function ξ_i is replaced by ξ_{in} as defined in (9).

With the formal expression for the compressibility factor of mixtures of non-additive hard spheres (8) and (10) it is now possible to derive the expressions for the scaling functions b_j and b_k. A low density expansion of (8) yields $Z=1+B_2^\mathrm{appr}\varrho+C_3^\mathrm{appr}\varrho^2$ with

$$B_2^\mathrm{appr}=\Gamma/\varrho+\frac{18}{\pi}\sum_i x_i\,\xi_{i1}\,\xi_{i2}/\varrho^2 \tag{11 a}$$

and

$$\begin{aligned}C_3^\mathrm{appr}=\sum_i x_i\Bigg[\frac{1}{3}(2\Gamma^2+\xi_{i3}^2)\\ +\frac{12}{\pi}\,\xi_{i1}\,\xi_{i2}(\Gamma+2\xi_{i3})+\frac{18}{\pi}\,\xi_{i2}^3\Bigg].\end{aligned} \tag{11 b}$$

It can be shown that up to the first order in α the condition $B_2=B_2^\mathrm{appr}$ reduces to

$$E_{jk}\,b_j+E_{kj}\,b_k=R_{jk}^2 \tag{12 a}$$

with

$$E_{jk}=(1+3x_j)\,R_j^2+2x_k\,R_jR_k+x_k\,R_j^2\,.$$

Similarly, up to the first order in α the condition $C_3=C_3^\mathrm{appr}$ reduces to

$$F_{jk}\,b_j+F_{kj}\,b_k=H_{jk} \tag{12 b}$$

with

$$\begin{aligned}F_{jk}=(x_j+9x_j^2)\,R_j^5+5x_j\,x_k(R_j^4\,R_k+2R_j^3\,R_k^2)\\ +4x_k\,R_j^2\,R_k^3+x_k^2(5R_j\,R_k^4+R_k^5)\end{aligned}$$

and

$$\begin{aligned}H_{jk}=x_k(R_k^5+5R_j\,R_k^4+4R_j^2\,R_k^3)\\ +x_j(R_j^5+5R_j^4\,R_k+4R_j^3\,R_k^2)\,.\end{aligned}$$

The parameters b_j and b_k can be obtained straightforwardly from (12). Using these b_j and b_k combined with (9) and (8) (or 10) the thermodynamics can be calculated. For symmetric mixtures (12) reduces to

$$b_j+b_k=1\,. \tag{13}$$

Thus for symmetric mixtures there is some freedom in the choice of b_j and b_k. However b_j should fulfill the boundary condition that it approaches 1 when x_k approaches 1. And furthermore, due to the symmetry, one should have $b_j=b_k=0.5$ when $x_j=x_k=0.5$. In principle it is possible to make one of the virial coefficients more accurate using (13). However such an approach is restricted to symmetric mixtures and will not be considered here. In the next section the predictions of the present equation of state with $b_j=1-x_j$

are compared with the results of computer calculations.

Results

Several groups have used MC or MD to calculate the compressibility factor Z for binary mixtures of non-additive hard spheres [15–20]. Most of these computer calculations have been carried out for equimolar symmetric mixtures. For the following discussion the mixtures are characterized by the non-additivity parameter $\Delta = \alpha/(R_1 + R_2)$ and the reduced densities $\varrho \sigma^3 = \varrho R_{11}^3$.

In Table 1 the predictions of the present theory for different symmetric non-additive mixtures are compared with MC-results [15, 17] and the predictions of two other theories: the MIX1 perturbation theory [16, 21–23] and an equation of state obtained recently by using a closure of the Ornstein-Zernike equation [17]. The MIX1 equation of state is of particular interest since it gives an accurate prediction of the critical point of symmetric mixtures with $\Delta = 0.2$ [24]. Furthermore, the MIX1 equation has recently been used with moderate success as a hard sphere reference in an equation of state for mixtures of Lennard-Jones particles [22].

At low densities ($0 \leq \varrho \sigma^3 \leq 0.2$) all theories give practically the same results (except for $\Delta = -0.2$, where the prediction of the MIX1 theory is a few percent to low compared with the MC results [15]). In Table 1 only results at higher densities are considered. From Table 1 it can be seen that the present theory on the Carnahan-Starling level ($\theta = 1$) is successful in describing the MC results for $\Delta = -0.05$ and $\Delta = 0.05$. These findings contrast the results for larger non-additivities $|\Delta| \geq 0.1$, where the equation of state on the virial level ($\theta = 3$) is superior to the Carnahan-Starling version. Apparently, in an optimized version of this theory, the value of θ has to be chosen to be dependent on $|\Delta|$. (It should be remembered that θ has a phenomenological role in the refined theories of additive hard sphere mixtures [11].)

For mixtures with negative non-additivities both versions of the present theory ($\theta = 1$ and $\theta = 3$) give better predictions of the compressibility factor than the MIX1 theory. For positive non-additivities the predictions of the MIX1 theory are in better agreement with the MC-data, than for $\Delta < 0$. The theory of Gazzillo and Pastore [17] yields good results for both positive and negative non-additivities. At higher densities their equation of state predicts the best compressibility factor of all the theories that are considered here. Unfortunately their theory is at present restricted to equimolar symmetric mixtures.

Table 1. Comparison of the theoretical and MC results for the compressibility factor Z of equimolar symmetric mixtures of non-additive hard spheres. Z (GaPa): [17], Z (mix1): [16], Z ($\theta = 1$), this work with $\theta = 1$, Z ($\theta = 3$), this work with $\theta = 3$; [a] [17], [b] [15].

Δ	$\varrho\sigma^3$	Z (MC)	Z (GaPa)	Z (mix1)	Z ($\theta=1$)	Z ($\theta=3$)
0.10	0.4	2.93 [a]	2.94	2.90	2.98	2.91
	0.6	5.32 [a]	5.42	5.36	5.68	5.29
0.05	0.4	2.74 [a]	2.72	2.71	2.73	2.68
	0.6	4.84 [a]	4.85	4.82	4.89	4.62
	0.8	9.08 [a]	9.25	9.22	9.49	8.37
−0.05	0.4	2.33 [a]	2.34	2.33	2.34	2.31
	0.6	3.80 [a]	3.78	3.75	3.80	3.66
	0.8	6.40 [a]	6.40	6.28	6.49	5.97
−0.10	0.4	2.17 [b]	2.18	2.14	2.19	2.17
	0.6	3.39 [b]	3.36	3.21	3.42	3.31
	0.8	5.22 [b]	5.34	4.82	5.55	5.18
	1.0	8.63 [b]	8.78	6.84	9.49	8.37
−0.20	0.4	1.95 [a]	1.95	1.75	1.96	1.95
	0.6	2.76 [a]	2.77	2.13	2.85	2.79
	0.8	3.95 [b]	3.98	1.88	4.27	4.07
	1.0	5.60 [b]	5.81	−1.61	6.62	6.07

Table 2. Comparison of the theoretical and MC results for the compressibility factor Z of asymmetric mixtures of non-additive hard spheres with $R_1 = (5/4) R_2, \Delta = -0.444$, $x_1 = 0.333$. Z (MC): [20], Z (mix1): [16, 22], Z ($\theta = 1$), this work with $\theta = 1$, Z ($\theta = 3$), this work with $\theta = 3$.

ϱ^*	Z (MC)	Z (mix1)	Z ($\theta=1$)	Z ($\theta=3$)
0.675	2.35	−1.49	2.35	2.32
1.289	5.35	< −167.2	6.21	5.70

$\varrho^* = \varrho (x_1 R_{11}^3 + x_2 R_{22}^3)$.

Next, the present theory is compared with the theories that are tested in [15]. For $\Delta \leq -0.1$ the virial equation ($\theta = 3$) the virial equation ($\theta = 3$) yields results that are comparable with the BH1-perturbation theory, while the equation of state with ($\theta = 1$) yields results that fall between the BH1-theory and the vdW1-theory [15]. However, the BH1- and the vdW1-theory do not fulfill the boundary conditions (i) and (ii) and therefore it is to be expected that these theories fail at small mole fractions.

So far not many data have been published for mixtures with $R_1 \neq R_2$. Ballone et al. [20] have published results for two states for the mixtures with $R_2 = 0.8 R_1$

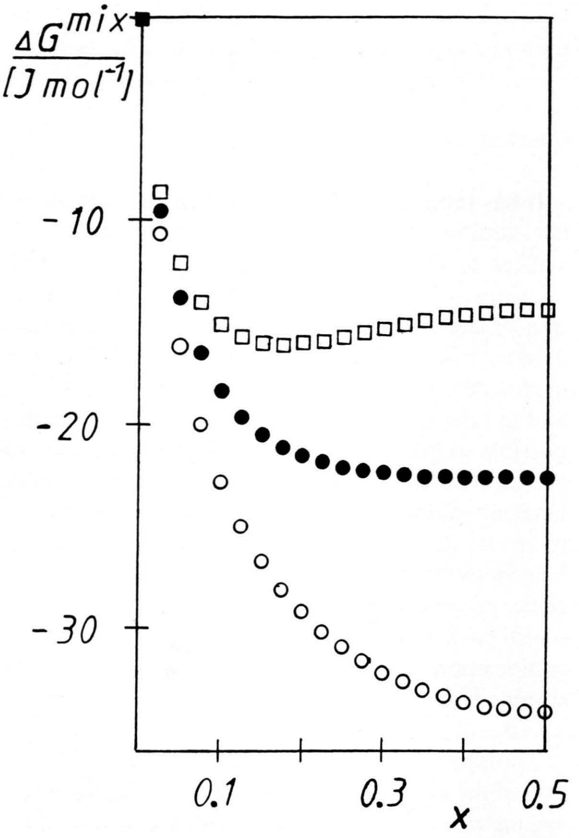

Fig. 1. The composition dependence of the excess Gibbs free energy of mixing at a constant pressure of a binary mixture of non-additive hard spheres with $R_j = R_k$ and $\Delta = 0.2$. Upper curve: $p^* = 1.2983$ (demixed);* middle curve: $p^* = 1.1624$ (critical); lower curve: $p^* = 0.9813$ (homogeneous).

and $\Delta = -0.444$. In Table 2 the predictions of the MIX1 and the present equations of state are tested against the results of [20]. The fair agreement between the present equation of state and MC is quite surprising in view of the relatively large value of Δ. The MIX1 equation of state is no longer valid at these states.

When the non-additivity parameter Δ is positive and sufficiently large, a phase-separation may occur at high pressure [16, 18, 19, 23]. The coexistence curve predicted by the theory can be calculated from the double tangent construction of the excess Gibbs free energy of mixing at a constant temperature and pressure

$$\Delta G^{\mathrm{mix}}(x_j) = G^{\mathrm{mix}}(x_j) - x_j\, G(x_j = 1) - (1 - x_j)\, G(x_j = 0)\,. \tag{16}$$

The mean molar Gibbs free energy can be calculated from the chemical potentials $G = \sum_i x_i\, \mu_i$. The relevant

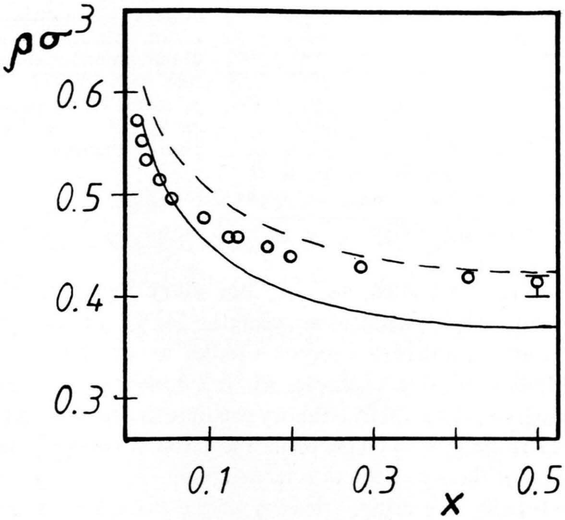

Fig. 2. The phase diagram of a binary mixture of non-additive hard spheres with $R_j = R_k$ and $\Delta = 0.2$. Drawn curve: this work with $\theta = 3$; dashed curve: MIX1 equation of state; dots: Gibbs ensemble MC [24].

thermodynamic quantities are obtained as functions of the pressure using the following procedure. First p, Z, and G are calculated at constant composition as a function of the density ϱ. Then ϱ, Z and G are recalculated as functions of the pressure using a spline-interpolation [25]. Usually, in the first part of the calculation the density-interval under consideration was divided into 100 gritpoints. The accuracy of the interpolation has been tested.

Figure 1 shows for several reduced pressures $p^* = p\sigma^3/k_B T$ the composition-dependence of ΔG^{mix} for the symmetric mixture with a relatively large $\Delta = 0.2$. Due to the symmetry of the mixture it suffices to show only the results for the mole fractions $0.0 \le x \le 0.5$. It is clear from Fig. 1 that demixing occurs at sufficiently high pressures. The corresponding $\varrho\sigma^3 - x$ phase diagram is shown in Fig. 2, where a comparison is made with Gibbs-ensemble MC-calculations [24]. For $x \le 0.07$ there is very good agreement between the present theory and the MC-data. This must of course be attributed to the implementation of the boundary conditions (i) and (ii). For large mole fractions the present equation of state predicts somewhat too low demixing densities. The prediction of the MIX1-theory is also shown in Figure 2. Whereas the MIX1 theory gives an accurate prediction of the critical point, it produces somewhat worse results at mole fractions $x < 0.15$. This is due to the fact that the

Method	$\varrho_c \sigma_{jj}^3$	Ref.
MC	0.415	[21]
SPT1	none?	[5]
SPT2	0.376	[4]
$\theta = 3$	0.369	this work
$\theta = 1$	0.355	this work
$\theta = 0$	0.352	this work

Table 3. Comparison of the critical density of the symmetric mixture with $\Delta = 0.2$ as predicted by the present theory and scaled particle theories.

MIX1 theory does not obey boundary conditions (i) and (ii). The differences between the MIX1-theory and the present theory become smaller at smaller non-additivities. For example, for a symmetric mixture with $\Delta = 0.1$ the MIX1-theory predicts the critical density to be $\varrho_c \sigma^3 = 0.604$ while the virial version of the present theory predicts $\varrho_c \sigma^3 = 0.589$.

Finally, the critical density of the symmetric mixture with $\Delta = 0.2$ as predicted by the present theory is compared in Table 3 with results of scaled particle theories [4, 5]. Tenne and Bergmann [5] did not find a phase separation for this non-additivity. This is possible because they tried to detect the phase transition by looking for a maximum in the density-dependence of the compressibility factor Z. The theory presented here does predict for this mixture a tiny local maximum in the density dependence of Z at the critical density. However such a maximum is not found with the present theory at the phase transition for the symmetric mixture with $\Delta = 0.1$. The criterion that Tenne and Bergmann have used for detecting the phase separation is not correct [4] since their criterion is not related to the true condition for phase separation: the equality of the chemical potentials.

Also from Table 3 it can be seen that the critical density predicted by the present theory is quite to the prediction of Bearman and Mazo [4]. The theory of Bearman and Mazo is designed for small and large non-additivities, whereas the present theory is valid for small values of Δ. This might explain why the present theory predicts a slightly poorer critical density of the mixture with the relatively large $\Delta = 0.2$ than the theory of [4]. However it should be noted that the Bearman-Mazo theory predicts that the thermodynamics of the one component fluid depends on the non-additivity of the mixture [4]. Therefore their theory is expected to fail at small mole fractions.

Conclusions

It has been shown here that the incorporation of a few additional limiting thermodynamic conditions suffices to derive of a simple equation of state for mixtures of non-additive hard spheres, when the equation of state for mixtures of additive hard spheres is used as a starting point. The limiting conditions used in this derivation are (i) $x_j \to 0$, (ii) $x_j \to 1$, (iii) $\alpha \to 0$, and (iv) the low density limit. Using these limits it is possible to derive an approximate expression for the chemical potential. The usage of two composition dependent scaling parameters of the mixture is essential to ensure that the chemical potential has the correct behaviour for the limits mentioned above. This feature of the present theory is in sharp contrast to common scaled particle approaches [4, 5], which have only one composition independent scaling parameter. The common scaled particle theories are not correct for $x_j \to 0$ and $x_j \to 1$ [4].

The equation of state which is obtained by integration of the Gibbs-Duhem equation is valid for binary symmetric and asymmetric mixtures of non-additive hard spheres with not to large non-additivities. For very small non-additivities of $|\Delta| \leq 0.05$ the Carnahan-Starling version of the present theory gives good agreement with computer data. For large non-additivities the virial version works better than the Carnahan-Starling version.

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