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PERTURBATION THEORY OF LIQUIDS WITH DOUBLE REFERENCE SYSTEM FOR MIXTURES WITH NON-ADDITIVE DIAMETERS*,**

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Perturbation expansion of the equation of state of a binary fluid mixture, based on two separate reference systems, is constructed. As the reference systems both pure components are taken. This theory describes very well the mixture of hard spheres with nonadditive diameters at high negative values of nonadditivity parameter. The theory is also extended to include, as the third reference system, the interactions between different species only (Widom-Rowlinson model). Perturbation corrections are given in this case by the overlap of all three different types of interactions. It is found that the inclusion of the third reference system extends the range of applicability of the theory to smaller values of the non additivity parameter.

1. *Introduction*

Simple single-component fluids and binary additive mixtures are correctly described by the perturbation theories of various types recently used [1, 2]. These expansions have also been applied to binary systems of nonadditive hard spheres [3, 4] where the collision diameter between spheres of two species is given by:

$$d_{AB} = \tfrac{1}{2}(d_{AA}+d_{BB})(1+\Delta), \tag{1}$$

with $\Delta \neq 0$ and d_{AA}, d_{BB} being the diameters of spheres of A and B species, respectively. The most studied systems have been these in which Δ is negative, over a range from -0.1 to -0.5 [3]. Comparison of equations of state obtained from the Monte Carlo calcula-

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tions, and from the conformal solution theory [5–8] or the theory of Leonard, Henderson, and Barker [9] shows that none of the perturbation theories is useful at large negative values of Δ (except when the density is very low).

The perturbation theories used so far for the description of binary systems are based on the knowledge of one reference fluid being either a pure fluid or a binary system of additive hard spheres. This work has been partly inspired by Henderson's review article [10], where the idea of a simultaneous expansion around both pure components of a mixture is implied, although not stated explicitly. In the second Section we shall present an expansion around two pure components of binary system. This expansion called by us the expansion around a double reference system shall be applied to nonadditive mixtures of hard spheres at very low Δ. In the third Section we shall propose an expansion about a triple reference system, treating every type of pair interactions in the binary system as one reference system. This approach shall be also applied to binary mixtures of additive hard spheres when the diameter of one species is much greater than that of the second species.

2. Expansion around two reference fluids

Let the mixture be composed of the particles of species A and B with the chemical potentials μ_A and μ_B, respectively, and be kept in a constant volume V and at a constant temperature T. Total potential energy $\Phi(\boldsymbol{r}^N)$ is decomposed as follows:

$$\Phi(\boldsymbol{r}^N) = \Phi_A(\boldsymbol{r}^{N_A})+\Phi_B(\boldsymbol{r}^{N_B})+\Phi_{AB}(\boldsymbol{r}^N), \tag{2}$$

where $\boldsymbol{r}^{N_A}$, $\boldsymbol{r}^{N_B}$ denote configuration spaces of species A, B, respectively, and $\boldsymbol{r}^N = \boldsymbol{r}^{N_A}\times \boldsymbol{r}^{N_B}$. We shall treat interactions between different species, Φ_{AB}, as perturbation imposed on system with no interactions between different particles, for which potential energy is $\Phi_A+\Phi_B$. The interactions are assumed to be pairwise-additive,

$$\Phi = \sum_{i,j} \varphi(r_{ij}), \tag{3}$$

and the obtained results will be applied to mixtures of hard spheres, with pair interactions:

$$\varphi(r_{ij}) = \begin{cases} \infty, & r_{ij} < d_{ij} \\ 0, & r_{ij} > d_{ij} \end{cases}, \tag{4}$$

d_{ij} being the contact diameter between particles i and j, although he theory is applicable to any interactions. For hard spheres with nonadditive diameters given by Eq. (1), the perturbation Φ_{AB} vanishes identically for $\Delta = -1$.

The grand partition function is given by:

$$\Xi = \sum_{N_A=0}^{\infty}\sum_{N_B=0}^{\infty} \frac{z_A^{N_A} z_B^{N_B}}{N_A!N_B!} Z_Q(T, V, N_A, N_B), \tag{5}$$

where summing is over variable number of particles A and B, z_A and z_B are the fugacities, and $Z_Q(T, V, N_A, N_B)$ is the canonical configuration integral:

$$Z_Q(T, V, N_A, N_B) = \int_V dr^{N_A} dr^{N_B} \exp(-\Phi_N/kT). \tag{6}$$

Expanding Ξ around the reference system we get the following expression for the equation of state:

$$\frac{pV}{kT} = \frac{p_{0A}V}{kT} + \frac{p_{0B}V}{kT} + \frac{p_{AB}V}{kT}, \tag{7}$$

where

$$\frac{p_{0K}V}{kT} = \ln \Xi_K = \ln\left(\sum_{N_K=0}^{\infty} \frac{z_K^{N_K}}{N_K!} Z_Q(T, V, N_K)\right), \tag{8}$$

for $K = A$ or B. Here p_{AB} represents the correction to the total pressure of the mixture due to the interactions between particles of different types, and is expressed by:

$$\frac{p_{AB}V}{kT} = \ln \langle \exp(-\Phi_{AB}/kT)\rangle_0. \tag{9}$$

The average is taken over the grand canonical ensemble of the unperturbed system, $\Phi_A + \Phi_B$. For Φ_{AB} pairwise-additive, we can express the correction p_{AB} as the series of averages of products of Mayer functions f_{AB}

$$f_{AB} = \exp(-\varphi_{AB}/kT) - 1.$$

Up to second order in f_{AB} this series is

$$\frac{p_{AB}V}{kT} = \left\langle \sum_{N_A} \sum_{N_B} f_{AB} \right\rangle_0 + \langle \sum_{N_A} \sum_{N_B} f_{AB}^2 \rangle_0 - \tfrac{1}{2}[\langle \sum_{N_A} \sum_{N_B} f_{AB} \rangle_0]^2 + O(\langle f_{AB}^3 \rangle_0). \tag{10}$$

Using the h-particle distribution functions (defined in the grand canonical ensemble) of the reference systems

$$n_{0K}^{(h)}(r_1, \ldots, r_h) = \left(\frac{\langle N_K \rangle}{V}\right)^h g_{0K}^{(h)} = \frac{1}{\Xi_K} \sum_{N_K=h}^{\infty} \frac{z_K^{N_K}}{(N_K-h)!} \int_V \exp(-\Phi_{N_K}/kT) dr^{N_K-h}, \tag{11}$$

where $K = A$ or B, we get, according to Eqs. (7) and (10), the following expression for the equation of state

$$\begin{aligned}\frac{pV}{kT} = \frac{p_{0A}V}{kT} + \frac{p_{0B}V}{kT} + \int n_{0A}^{(1)}(\boldsymbol{r}_1)n_{0B}^{(1)}(\boldsymbol{r}_2)f_{AB}(\boldsymbol{r}_1, \boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\ +1/2 \int n_{0A}^{(1)}(\boldsymbol{r}_1)n_{0B}^{(2)}(\boldsymbol{r}_2, \boldsymbol{r}_3)f_{AB}(\boldsymbol{r}_1, \boldsymbol{r}_2)f_{AB}(\boldsymbol{r}_1, \boldsymbol{r}_3)d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 \\ +1/2 \int n_{0A}^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_3)n_{0B}^{(1)}(\boldsymbol{r}_2)f_{AB}(\boldsymbol{r}_1, \boldsymbol{r}_2)f_{AB}(\boldsymbol{r}_2, \boldsymbol{r}_3)d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 \\ +1/2\Big[\int n_{0A}^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_3)n_{0B}^{(2)}(\boldsymbol{r}_2, \boldsymbol{r}_4)f_{AB}(\boldsymbol{r}_1, \boldsymbol{r}_2)f_{AB}(\boldsymbol{r}_3, \boldsymbol{r}_4)d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 d\boldsymbol{r}_4 \\ - \int n_{0A}^{(1)}(\boldsymbol{r}_1)n_{0B}^{(1)}(\boldsymbol{r}_2)f_{AB}(\boldsymbol{r}_1, \boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \int n_{0A}^{(1)}(\boldsymbol{r}_3)n_{0B}^{(1)}(\boldsymbol{r}_4)f_{AB}(\boldsymbol{r}_3, \boldsymbol{r}_4)d\boldsymbol{r}_3 d\boldsymbol{r}_4\Big]. \qquad (12)\end{aligned}$$

The distribution functions in Eq. (12) are functions of the activities. Conversion of this expansion into a power series of average density, together with the thermodynamic limit $V \to \infty$, leads to the following result:

$$\begin{aligned}\frac{pV}{NkT} = x_A \frac{p_{0A}V}{N_A kT} + x_B \frac{p_{0B}V}{N_B kT} - x_A x_B \varrho \int f_{AB}(\boldsymbol{r}_{12})d\boldsymbol{r}_{12} \\ - x_A x_B^2 \varrho^2 \int f_{AB}(\boldsymbol{r}_{12})f_{AB}(\boldsymbol{r}_{13})h_{0B}(\boldsymbol{r}_{23})d\boldsymbol{r}_{12}d\boldsymbol{r}_{23} \\ - x_A^2 x_B \varrho^2 \int h_{0A}(\boldsymbol{r}_{13})f_{AB}(\boldsymbol{r}_{12})f_{AB}(\boldsymbol{r}_{32})d\boldsymbol{r}_{12}d\boldsymbol{r}_{23} \\ -3/2 x_A^2 x_B^2 \varrho^3 \int h_{0A}(\boldsymbol{r}_{13})h_{0B}(\boldsymbol{r}_{24})f_{AB}(\boldsymbol{r}_{12})f_{AB}(\boldsymbol{r}_{34})d\boldsymbol{r}_{12}d\boldsymbol{r}_{23}d\boldsymbol{r}_{34}, \qquad (13)\end{aligned}$$

where $\varrho = N/V$, and h_{0A} h_{0B} are the two-particle correlation functions of the reference systems

$$h_{0K} = \frac{1}{\varrho_K^2} n_{0K}^{(2)} - 1, \quad K = A, B$$

being now the functions of partial densities $\varrho_K = N_K/V$ instead of activities z_K.

Equation (13) represents the second order expansion around both pure components of the mixture. The higher-order terms depend on the three- and more-particle distribution functions of the reference systems.

The above calculation may be easily generalized for a multicomponent mixture.

3. *An expansion about a triple reference system*

The perturbation expansion presented in the previous Section is expected to fail for the additive mixtures and for the mixtures showing a positive departure from additivity (positive Δ).

A perturbation expansion for a general mixture should take into account all types of interactions in the same degree. Thus, a perturbation expansion for a binary system ought, to within zeroth order, to include two fluids of pure components and a fluid in which there are only interactions between particles of different species (the latter fluid is the model of Widom and Rowlinson [11–15]). Terms of higher orders of this expansion will appear from the overlapping of all three reference systems, i. e. from the overlapping of all interactions in the mixture. In this Section we shall find such an expansion.

The derivation of the expansion is based on the known procedure of renormalization of the diagrammatic expression for the virial expansion [16–21]. Performing this renormalization by the summation of the diagrammatic lines corresponding to pure components of the mixture, we get two types of renormalized lines being the correlation functions of pure components. Next, we perform the summations of diagrammatic substructures built of the lines being only the Mayer functions of the pair interactions between the particles of different types, which leads to the correlation functions $h_{0AB}^{(IK)}$ of the Widom-Rowlinson fluid. In this way we get the following expression for the equation of state, written up to the two-particle correlation functions of the three reference systems

$$\begin{aligned}\frac{pV}{NkT} &= x_A\left(\frac{pV}{N_AkT}\right)_{0A}+x_B\left(\frac{pV}{N_BkT}\right)_{0B}+\left(\frac{pV}{NkT}-1\right)_{0AB}\\ &-x_B^2\varrho\int h_{0B}(\boldsymbol{r}_1,\boldsymbol{r}_2)h_{0AB}^{(BB)}(\boldsymbol{r}_1,\boldsymbol{r}_2)d\boldsymbol{r}_1-x_A^2\varrho\int h_{0A}(\boldsymbol{r}_1,\boldsymbol{r}_2)h_{0AB}^{(AA)}(\boldsymbol{r}_1,\boldsymbol{r}_2)d\boldsymbol{r}_1\\ &-3/2x_A^2x_B^2\varrho^3\int h_{0A}(\boldsymbol{r}_1,\boldsymbol{r}_2)h_{0B}(\boldsymbol{r}_3,\boldsymbol{r}_4)h_{0AB}^{(AB)}(\boldsymbol{r}_1,\boldsymbol{r}_3)h_{0AB}^{(AB)}(\boldsymbol{r}_2,\boldsymbol{r}_4)d\boldsymbol{r}_1d\boldsymbol{r}_2d\boldsymbol{r}_3, \qquad (14)\end{aligned}$$

with $h_{0AB}^{(IK)}$ being a sum of all topologically different connected diagrams built of two root points corresponding to particles of species I and K, and of f_{AB}-lines only.

4. *Numerical results*

The results of the Monte Carlo (MC) simulations for mixtures of hard spheres with non-additive contact distances were given by Adams and McDonald [3] for the mixture of two identical species in equal concentrations. In this work we have performed the calculation for such mixtures for $\Delta = -0.3$, -0.4, and -0.5. The use of the approximation (13) requires the knowledge of the equation of state and of the radial distribution function of one-component hard-sphere fluid. We have used the Carnahan-Starling equation of state [21] and the analytic formulas of Mandel et al. [23] for the radial distribution function. The use of the perturbation expansion around triple reference system, Eq. (14), requires the knowledge of the properties of the third reference fluid, for which $\Phi_{AA} = \Phi_{BB} = 0$, $\Phi_{AB} \neq 0$. The model of this kind was considered in the literature only for the mixture of hard spheres: this is the so-called Widom-Rowlinson model (WR), described by the parameters

$$d_A = d_B = 0, \qquad d_{AB} = \alpha > 0.$$

According to Ref. [14], the pressure of this system is given by the relations:

$$\begin{aligned}\frac{p^{\mathrm{v}}}{kT} &= \varrho_A+\varrho_B+\eta^2(1-0.24285\,\eta^2+0.08714\,\eta^4-0.03908\,\eta^6\\ &\quad+0.01969\,\eta^8-0.01145\,\eta^{10}+0.00785\,\eta^{12}-\ldots), \qquad (15)\end{aligned}$$

$$\begin{aligned}\frac{p^{\mathrm{c}}}{kT} &= \varrho_A+\varrho_B+\eta^2(1-0.16190\,\eta^2+0.04665\,\eta^4-0.01721\,\eta^6\\ &\quad+0.00732\,\eta^8-0.00386\,\eta^{10}+0.00216\,\eta^{12}-\ldots), \qquad (16)\end{aligned}$$

where p^{v} and p^{c} denote the pressures calculated from the virial and compressibility equations of state, and

$$\eta = 2\pi\alpha^3\sqrt{\varrho_A\varrho_B}\,, \qquad (\eta/2\pi\alpha^3) \leqslant 1.7.$$

Eqs. (15) and (16) predict different values of the pressure; hence we have used in our calculations the Carnahan-Starling-type weighted average:

$$3p_{0AB} = 2p^{\mathrm{v}}+p^{\mathrm{c}}. \tag{17}$$

Closed expressions for two-particle correlation functions of the WR model are not known, and we have used the lowest-order approximations

$$\begin{aligned} h_{0AB}^{(AB)}(\mathbf{r}_1, \mathbf{r}_2) &= f_{AB}(\mathbf{r}_1, \mathbf{r}_2), \\ h_{0AB}^{(AA)}(\mathbf{r}_1, \mathbf{r}_2) &= x_B\varrho \int f_{AB}(\mathbf{r}_1, \mathbf{r}_3)f_{AB}(\mathbf{r}_3, \mathbf{r}_2)d\mathbf{r}_3, \\ h_{0AB}^{(BB)}(\mathbf{r}_1, \mathbf{r}_2) &= x_A\varrho \int f_{AB}(\mathbf{r}_1, \mathbf{r}_3)f_{AB}(\mathbf{r}_3, \mathbf{r}_2)d\mathbf{r}_3. \end{aligned} \tag{18}$$

TABLE I

pV/NkT of the mixture of hard spheres with nonadditive diameters, for $x_A = x_B = 0.5$

ϱ^*	MC	BH1	BH2	VDW1	VDW2	MIX1	MIX2	Eq. (13)	Eq. (14)
					$\Delta = -0.3$				
0.2	1.31	1.30	1.33	1.34	1.33	1.21	1.30	1.33	1.36
0.4	1.80	1.73	1.76	1.82	1.76	1.33	1.58	1.74	1.81
0.6	2.43	2.33	2.31	2.54	2.30	1.14	1.73	2.27	2.36
0.8	3.12	3.19	2.99	3.60	2.94			2.94	3.03
1.0	4.25	4.46	3.74	5.25	3.54			3.80	3.90
1.2	5.73	6.38	4.36	7.89	3.67			4.93	5.03
1.4	7.89	9.40	4.23	12.34	1.95			6.26	6.57
					$\Delta = -0.4$				
1.0	3.69	3.37	2.86	4.38	2.46			3.58	3.66
1.2	4.99	4.46	3.02	6.24	1.84			4.66	4.75
1.4	6.53	6.00	2.56	9.14	−0.79			5.99	6.09
					$\Delta = -0.5$				
0.2	1.26	1.20	1.26	1.27	1.26	0.99	1.26	1.27	1.28
0.4	1.61	1.45	1.55	1.65	1.54	0.53	1.24	1.61	1.64
0.6	2.06	1.76	1.87	2.16	1.82	−0.96	0.62	2.06	2.10
0.8	2.65	2.16	2.17	2.86	1.99			2.64	2.69
1.0	3.40	2.66	2.41	3.86	1.84			3.42	3.47
1.2	4.61	3.32	2.47	5.31	0.88			4.45	4.53
1.4	5.92	4.17	2.12	7.45	−1.99			5.84$^+$	5.92$^+$
1.6	8.10	5.31	0.96	10.75	−9.28			7.86$^+$	7.94$^+$

The results are presented in Table I and in Figs. 1 and 2, where ϱ^* is the reduced density

$$\varrho^* = \varrho d^3, \tag{19}$$

d being the hard-sphere diameter. Together with results obtained from Eqs. (13) and (14) are presented, for comparison, the MC data and the results obtained by Adams and

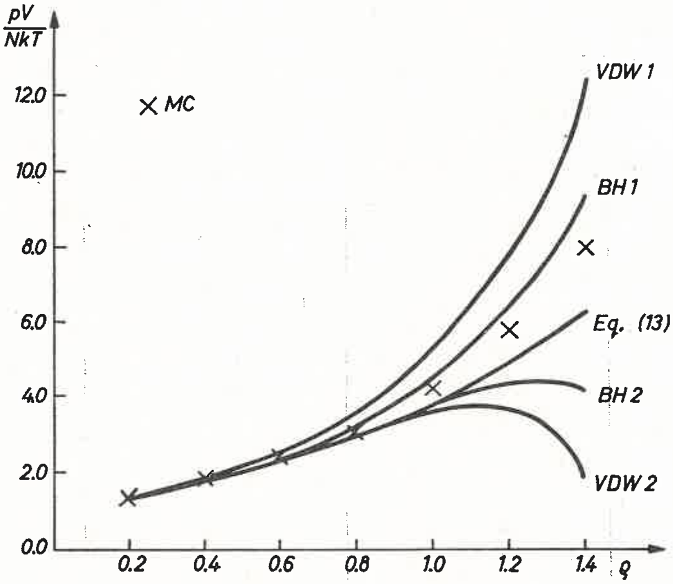

Fig. 1. The equation of state for the mixture of hard spheres with nonadditive diameters, for $\Delta = -0.3$; $x_A = x_B = 0.5$

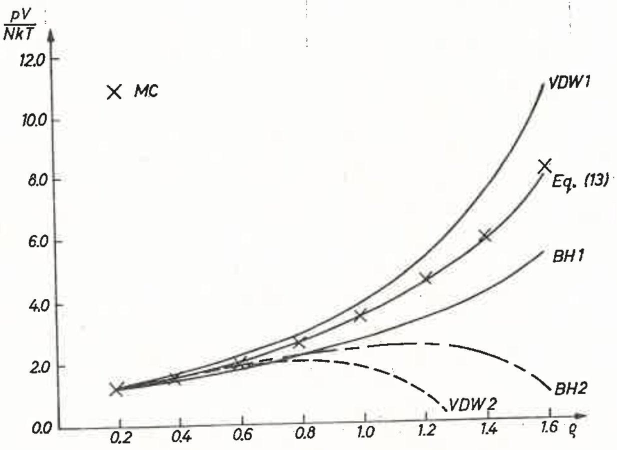

Fig. 2. The equation of state for the mixture of hard spheres with nonadditive diameters, for $\Delta = -0.5$; $x_A = x_B = 0.5$

McDonald [3] from other perturbation theories. The data denoted by BH and VDW are the results of two versions of the conformal solution theory, where the reference system is the one-component fluid of hard spheres of diameter d_0, defined by

$$d_0^n = \sum_{i,j} x_i x_j d_{ij}^n, \tag{20}$$

with $n = 1$ for BH, and $n = 3$ for VDW version. The data denoted as MIX are obtained from the perturbation theory with the reference system being the mixture of hard spheres with additive diameters [9]. BH1, VDW1 and MIX1 versions are calculated from the first order, BH2, VDW2 and MIX2 — from the second order perturbation expansion.

TABLE II

pV/NkT of the mixture of hard spheres with additive diameters, for $x_A = x_B = 0.5$

ϱ^*	MC	BH2	Eq. (14)
$R = 1.1$			
0.1	1.239	1.239	1.284
0.3	1.96	1.964	1.921
0.5	3.17	3.260	2.968
$R = 5/3$			
0.1	1.220	1.219	1.261
0.3	1.85	1.869	1.910
0.5	3.04	3.037	2.780
$R = 3.0$			
0.3	1.739	1.696	1.772
0.5	2.69	2.543	2.597

We have performed also the calculations, based on the approximation (14) together with Eqs. (15)–(18), for the mixture of hard spheres with additive diameters with $R \equiv d_A/d_B = 1.1$, 5/3, and 3.0. The results are presented in Table II, together with the MC results and results obtained from the Barker-Henderson theory [5, 7]. The reduced density is defined here by:

$$\varrho^* = \varrho(x_A d_A^3 + x_B d_B^3). \tag{21}$$

5. *Final remarks*

The perturbation expansion around the double reference system, discussed in this paper, leads — within the second-order approximation — to correct results for the equation of state for nonadditive mixtures with high negative values of the nonadditivity parameter Δ.

The agreement with MC results is very good for $\Delta = -0.5$ and we thus may expect that the considered approximation will also be correct for $\Delta < -0.5$, where, however, no experimental data are available. There are small deviations at $\Delta = -0.4$ and -0.3; however, at $\Delta = -0.4$ our results are still better than those obtained from other theories. On the other hand, for $\Delta > -0.3$, other theories lead to more correct results. The inclusion of the third reference system, taking into account interactions between unlike particles, improves the results for strongly nonadditive mixtures only slightly. On the other hand, the theory based on triple reference system leads to relatively good results for additive mixtures of hard spheres with very different diameters. However, the lack of the exact correlation functions of the WR model makes impossible the full estimation of the usefulness of our triple-reference model.

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