CORRESPONDING STATES THEORY OF MIXTURES OF HARD SPHERES

K. Hlavatý

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague - Suchdol

Excess volumes and Gibbs free energies of several mixtures of hard spheres at constant pressure were calculated using the one-liquid and two-liquid versions of the corresponding states theory with different combination rules for the equivalent substance parameters and the results were compared with the Percus–Yevick compressibility equation for a mixture of hard spheres. New combination rules were found, which yield better agreement with the Percus–Yevick equation than the van der Waals combination rules proposed by Leland, Rowlinson and Sather.

The theory of liquid mixtures is still a tempting field for many semiempirical theories as there is no satisfactory rigorous treatment. Recently Barker and Henderson[1] and Toxvaerd and coworkers[2] have shown that by far the most important and radial distribution function determining part of any realistic intermolecular potential is its hard core part, the attractive part being only a background maintaining the high density of liquids. Leland and coworkers[3,4] proposed then a fairly successful corresponding states treatment of mixtures of hard spheres. They suggested combination rules for the equivalent substance parameters, which were identical with those used many years earlier by van der Waals in connection with his equation of state for gaseous mixtures. This work is an attempt to test the range of validity of Leland's treatment and to find some other combination rules which would predict properties of mixtures of hard spheres with equal or possibly better accuracy than those of Leland.

THEORETICAL

For a pure liquid with the intermolecular potential of the form

$$u(r) = f\varepsilon_{00}\varphi(r/g\sigma_{00}) \qquad (1)$$

and whose total configurational energy $\mathscr{U}$ may be written as a sum of pair interactions only

$$\mathscr{U} = \sum_{i<j} u(r_{ij}) \qquad (2)$$

the following relation for the configurational Helmholtz free energy F holds[5]

$$F(V, T) = fF_0(V/g^3, T/f) - 3NkT \ln g . \qquad (3)$$

In Eq. (1), φ is a common function for all liquids under consideration, r is the inter-molecular distance, ε_{00} and σ_{00} are the potential parameters of a reference substance, and f and g are parameters scaling the departure of the depth of the potential well and the intermolecular distance of a particular liquid from the respective properties of the reference substance potential. In Eq. (3), V is the molar volume, T is the absolute temperature, and F_0 is the configurational Helmholtz free energy of the reference substance. Analogically we may write for the configurational Helmholtz or Gibbs free energy of a mixture

$$F_x(V, T) = f_x F_0(V/g_x^3, T/f_x) - 3NkT \ln g_x , \qquad (4)$$

or

$$G_x(p, T) = f_x G_0(pg_x^3/f_x, T/f_x) - 3NkT \ln g_x . \qquad (5)$$

Here, f_x and g_x are corresponding scaling parameters of the mixture. They are analogues of f and g for pure liquids and are usually called the equivalent substance parameters. Eqs (4) and (5) are entirely equivalent but unfortunately they definitely do not hold exactly even when Eqs $(1)-(2)$ are satisfied unless it is assumed that f_x and g_x are functions of T and V. For practical purposes however, the dependence of f_x and g_x on T and V is usually discarded and both f_x and g_x are considered as functions of the composition only. Leland and coworkers[3] proposed for these parameters the following rules

$$f_x g_x^3 \equiv f_x h_x = \sum_{r, s=1}^{n} x_r x_s f_{rs} h_{rs} , \qquad (6)$$

$$h_x = \sum_{r,s} x_r x_s h_{rs} \quad \text{with} \quad h_{rs}^{1/3} = (h_{rr}^{1/3} + h_{ss}^{1/3})/2 . \qquad (7)$$

calling them the van der Waals approximation because of their identity with the combination rules used for the van der Waals equation of state for gaseous mixtures; x_r stands here for the mol fraction of the r-th component of the mixture and n is the number of present components.

Unlike the one-liquid corresponding states model expressed by Eqs $(4)-(5)$, the two-liquid model may be introduced by the equations[6]

$$F_x(V, T) = \sum_{r=1}^{n} x_r [f_{xr} F_0(V/h_{xr}, T/f_{xr}) - NkT \ln h_{xr}] , \qquad (8)$$

or

$$G_x(p, T) = \sum_{r=1}^{n} x_r \left[f_{xr} G_0(ph_{xr}/f_{xr}, T/f_{xr}) - NkT \ln h_{xr} \right]. \qquad (9)$$

The two versions given by Eqs (8) and (9) are not equivalent and in fact they yield completely different results. The volumes V/h_{xr} were introduced into Eq. (8) rather arbitrarily by an analogy with the Prigogine cell model[7]. On the other hand, Eq. (9) was obtained from Eq. (8) written with unspecified volumes V_r in place of V/h_{xr} by minimizing $F_x(V, T)$ with respect to V_r at constant T and V[7]. Therefore this second, or p, T version should be preferred from the theoretical point of view. A justification for Eq. (9) follows also from the following consideration on partial molar volumes. For the sake of simplicity we shall assume that all $f_{rs} = 1$. Then differentiating Eq. (8) we obtain

$$p = \sum_{r} (x_r/h_{xr}) \, p_0(V/h_{xr}), \qquad (10)$$

where the dependence on T was here omitted because of its irrelevance. For the partial molar volume we may write

$$\overline{V}_i = - (\partial V_t/\partial p)_x/(\partial n_i/\partial p)_V = - n_t(\partial p/\partial n_i)_V/(\partial p/\partial V)_x. \qquad (11)$$

where V_t is the total volume of the mixture $V_t = n_t V$ and $n_i = x_i n_t$. The index x denotes that the derivative is performed at constant composition. For the numerator in Eq. (11) it holds

$$n_t(\partial p/\partial n_i)_V = (\partial p/\partial x_i)_V - \sum_{r} x_r(\partial p/\partial x_r)_{V, x_k \neq x_r} \qquad (12)$$

and further

$$(\partial p/\partial x_i)_{V, x_k} = (1/h_{xi}) \, p_0(V/h_{xi}) - \sum_{j} (x_j/h_{xj}^2) \, p_0(V/h_{xj}) \, (\partial h_{xj}/\partial x_i) -$$
$$- \sum_{j} (x_j V/h_{xj}^3) \, (\partial p_0(V/h_{xj})/\partial(V/h_{xj})) \, (\partial h_{xj}/\partial x_i). \qquad (13)$$

If we assume further that

$$h_{xj} = h_{jj}, \qquad (14)$$

which will be shown later on to be a fairly good approximation, then Eq. (13) reduces to

$$(\partial p/\partial x_i)_{V, x_k} = (1/h_{ii}) \, p_0(V/h_{ii}). \qquad (15)$$

For a binary mixture, this leads immediately to

$$n_t(\partial p/\partial n_1)_V = x_2 \left[(1/h_{11}) \, p_0(V/h_{11}) - (1/h_{22}) \, p_0(V/h_{22}) \right]. \qquad (16)$$

Substituting it into Eq. (11) we obtain the result that either $\overline{V}_1 < 0$ or $\overline{V}_2 < 0$, which is obviously a nonsense. By a tedious algebra, the same result may be obtained with h_{xj} given by Eq. (31) for $m = 3$ and most probably with any other combination rule for h_{xj}.

On the other hand, differentiating Eq. (9) for V yields

$$V = \sum_r x_r h_{xr} V_0(ph_{xr}) \equiv \sum_r x_r h_{xr} V_{0r} . \tag{17}$$

Then

$$\overline{V}_i = V + (\partial V/\partial x_i) - \sum_r x_r (\partial V/\partial x_r) \tag{18}$$

and

$$(\partial V/\partial x_i) = h_{xi} V_{0i} + \sum_j x_j V_{0j}(\partial h_{xj}/\partial x_i) +$$
$$+ \sum_j x_j h_{xj}[\partial V_{0j}/\partial(ph_{xj})] p(\partial h_{xj}/\partial x_i) . \tag{19}$$

Taking into account Eq. (14) we obtain

$$(\partial V/\partial x_i) = h_{ii} V_{0i} \tag{20}$$

and finally

$$\overline{V}_i = h_{ii} V_0(ph_{ii}) , \tag{21}$$

which looks quite reasonably.

Leland and coworkers[4] proposed the combination rules for the two-liquid model in the form analogical to the one liquid model

$$f_{xr} h_{xr} = \sum_{s=1}^n x_s f_{rs} h_{rs} \tag{22}$$

and

$$h_{xr} = \sum_{s=1}^n x_s h_{rs} . \tag{23}$$

They tested their one-liquid model with the combination rule given by Eq. (7) on mixtures of soft spheres[3] and compared the results with the rather accurate[8] Percus–Yevick compressibility equation of state of a mixture of soft spheres[9,10]. They expanded the excess Helmholtz free energy F^E in powers of $\delta h = h - 1$ and found a good optical coincidence between the expansions of F^E for the Percus–Yevick compressibility equation and that based on Eqs (4) and (7). However, it may be shown that the respective expressions differ by as much as NkT in the range of the existence of liquids, which may be quite a large amount of energy. A definite disadvantage of their expansion method is that it is limited to $\delta h \to 0$, but at the same time the authors tried to arrive at some results applicable to molecules widely different in size.

A final remark should be made in connection with Eq. (7). This equation was proposed some 10 years ago by Leland and coworkers[3] and it was based on a perturbation treatment of the radial distribution function, which was expanded in powers of T^{-1} and all terms beyond the second were neglected[11]. Erroneously, the term leading to Eq. (7) was added in their paper quite arbitrarily to the expansion and therefore Eq. (7) must be regarded as an empirical expression, which is justified as any other empirical expression for h_x that satisfies correct limiting relations $\lim_{x_1 \to 1} h_x = h_{ii}$.

We decided to compare results of the corresponding states treatment expressed by Eqs (4), (8), and (9), on a mixture of hard spheres obeying the Percus–Yevick compressibility equation of state for several new rules for parameters h_x or h_{xr}. For a binary mixture of hard spheres, Eqs (4), (8) and (9) can be written discarding the dependence on T as

$$F_x(V) = F_0(V/h_x) - NkT \ln h_x, \tag{24}$$

$$F_x(V) = \sum_{r=1}^{2} x_r [F_0(V/h_{xr}) - NkT \ln h_{xr}], \tag{25}$$

and

$$G_x(p) = \sum_{r=1}^{2} x_r [G_0(ph_{xr}) - NkT \ln h_{xi}]. \tag{26}$$

The following rules for h_x were used

$$h_x = \left[\sum_{r,s} x_r x_s h_{rs}^{m/3}\right]^{3/m} \qquad \text{for} \quad m \in \langle 3,5 \rangle, \tag{27}$$

$$h_x = 1/4 \sum_{r,s} x_r x_s (2h_{rs} + h_{rr} + h_{ss}), \tag{28}$$

$$h_x = \left[\sum_{r} x_r h_{rr}^{n/3}\right]^{3/n} \qquad \text{for} \quad n \in \langle 1,3 \rangle, \tag{29}$$

and

$$h_x = \sum_{r,s} x_r x_s h_{rs} \quad \text{with} \quad h_{rs} = \left[1/2(h_{rr}^{2/3} + h_{ss}^{2/3})\right]^{3/2}. \tag{30}$$

Except for Eq. (30), the usual rule for h_{rs} given in Eq. (7) was assumed. Eqs (27) to (30) were used together with Eq. (24). For the two-liquid versions given by Eqs (25) and (26), the following rules were tested

$$h_{xr} = \left[\sum_{s} x_s h_{rs}^{m/3}\right]^{3/m} \quad \text{for} \quad m \in \langle 1,6 \rangle \tag{31}$$

and

$$h_{xr} = h_{rr}. \tag{32}$$

CALCULATIONS

Excess Gibbs free energies G^E and volumes V^E at constant pressure p were calculated for several binary mixtures of hard spheres for all proposed mixing rules and for both one- and two-liquid versions of the corresponding states theory according to the equations

$$G^E = G_x(p) - x_1 G_1(p) - x_2 G_2(p) \tag{33}$$

and

$$V^E = V(p) - x_1 V_1(p) - x_2 V_2(p) . \tag{34}$$

For the reference substance as well as for pure components, the Percus–Yevick compressibility equation of state of hard spheres[12] was used

$$\frac{pV_i}{NkT} = \frac{1 + y_i + y_i^2}{(1 - y_i)^3} \quad \text{with} \quad y_i = \pi N\sigma_{ii}^3/6V_i = \pi Nh_{ii}\sigma_{00}^3/6V_i , \tag{35}$$

where σ_{00} is the respective hard sphere diameter. For a given value of p, Eq. (35) was solved for V_i and the resulting V_i was substituted into the Percus–Yevick equation for the configurational part of G_i

$$\frac{G_i}{NkT} = -1 + \ln \frac{6y_i}{\pi\sigma_{ii}^3(1 - y_i)} + \frac{2 + 8y_i - 7y_i^2 + 3y_i^3}{2(1 - y_i)^3} . \tag{36}$$

Volumes V of the mixture at the given p were obtained from the pressure or volume derivatives of Eqs (24)−(26)

$$p = (1/h_x)\, p_0(V/h_x) , \tag{37}$$

$$p = \sum_{r=1}^{2} (x_r/h_{xr})\, p_0(V/h_{xr}) \tag{38}$$

and

$$V = \sum_{r=1}^{2} x_r h_{xr} V_0(ph_{xr}) . \tag{39}$$

The resulting volumes were then substituted into the respective equations for the Gibbs free energy and finally the values of the excess functions were calculated from Eqs (33) and (34).

The results were compared with similar calculations using the Percus–Yevick compressibility equation of state for the mixture of hard spheres[12]

$$\frac{p}{kT} = \frac{6}{\pi}\left[\frac{\xi_0}{(1 - \xi_3)} + \frac{3\xi_1\xi_2}{(1 - \xi_3)^2} + \frac{3\xi_2^3}{(1 - \xi_3)^3} \right] \tag{40}$$

with

$$\xi_k = (\pi N/6\,V) \sum_{r=1}^{2} x_r \sigma_{rr}^k . \tag{41}$$

The calculations were performed on the computer Minsk 22 for $p\sigma_{22}^3/kT \in \langle 1{\cdot}40 \rangle$, for $h_{11}/h_{22} = 0{\cdot}4;\, 0{\cdot}6,$ and $0{\cdot}8$, and for $x_1 \in \langle 0{\cdot}1,\, 0{\cdot}9 \rangle$.

DISCUSSION

We may see from Table I and Figs $1-4$ that the optimum value of m in Eq. (27) in the one-liquid version is $m = 4$. This compares well with the values of m determined by putting the difference between the Taylor expansions of the Percus–Yevick and the one liquid version[3] equal to zero; we found that $m = 3 \cdot 7 - 4 \cdot 1$ for $\pi N \sigma_{00}/6V = 0 \cdot 4 - 0 \cdot 6$. Eqs (28) and (30) and Eq. (29) for $n = 2 \cdot 5$ yield almost identical results which are only slightly worse; the latter results are not included in the tables. The results of the so called van der Waals approximation, that is of Eq. (27) for $m = 3$, are clearly in a considerable error, especially for larger differences in the hard sphere diameters of both components. It follows from Table III that the two-liquid (V, T) version of the corresponding states theory cannot be used for predicting properties of hard spheres with the combination rules given by Eqs (31) and (32). It is probably not worth trying to search for combination rules which could be used successfully with this

TABLE I

Thermodynamic Excess Functions for the Equimolar Binary Mixture of Hard Spheres According to the One-Liquid Theory of Corresponding States Expressed by Eq. (24) with the Combination Rules Given by Eqs $(27)-(30)$ at $p\sigma_{22}^3/kT = 12$ and $V_2/N\sigma_{22}^3 = 1 \cdot 07267$

| Type of Equation	$h_{11}/h_{22} = 0 \cdot 4$, $V_1/N\sigma_{11}^3 = 1 \cdot 36397$		$h_{11}/h_{22} = 0 \cdot 8$, $V_1/N\sigma_{11}^3 = 1 \cdot 13026$	
	$V^E/N\sigma_{22}^3$	G^E/NkT	$V^E/N\sigma_{22}^3$	G^E/NkT
Percus–Yevick Eq.	$-0 \cdot 00024$	$-0 \cdot 0267$	$-0 \cdot 00001$	$-0 \cdot 0017$
Eq. (27) for $m = 1$	$-0 \cdot 03089$	$-0 \cdot 4280$	$-0 \cdot 00248$	$-0 \cdot 0339$
2	$-0 \cdot 02094$	$-0 \cdot 2848$	$-0 \cdot 00170$	$-0 \cdot 0227$
3	$-0 \cdot 01106$	$-0 \cdot 1422$	$-0 \cdot 00092$	$-0 \cdot 0115$
3·5	$-0 \cdot 00617$	$-0 \cdot 0716$	$-0 \cdot 00052$	$-0 \cdot 0058$
3·9	$-0 \cdot 00229$	$-0 \cdot 0155$	$-0 \cdot 00021$	$-0 \cdot 0014$
4	$-0 \cdot 00132$	$-0 \cdot 0015$	$-0 \cdot 00013$	$-0 \cdot 0002$
5	$0 \cdot 00825$	$0 \cdot 1365$	$0 \cdot 00065$	$0 \cdot 0110$
Eq. (29) for $n = 1$	$-0 \cdot 03089$	$-0 \cdot 4286$	$-0 \cdot 00248$	$-0 \cdot 0339$
2	$-0 \cdot 01095$	$-0 \cdot 1405$	$-0 \cdot 00092$	$-0 \cdot 0115$
3	$0 \cdot 00867$	$0 \cdot 1426$	$0 \cdot 00065$	$0 \cdot 0110$
Eq. (30)	$-0 \cdot 00113$	$0 \cdot 0013$	$-0 \cdot 00013$	$-0 \cdot 0002$
Eq. (28)	$-0 \cdot 00118$	$0 \cdot 0004$	$-0 \cdot 00013$	$-0 \cdot 0002$
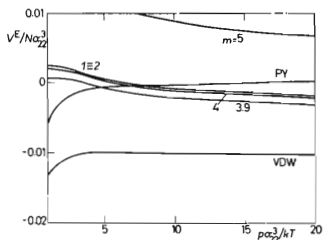
Fig. 1

Pressure Dependence of Excess Volumes of the Equimolar Mixture of Hard Spheres at $h_{11}/h_{22} = 0.4$ and $x_1 = 0.5$ for Different Combination Rules for h_x in the One-Liquid Corresponding States Theory and for the Percus–Yevick Compressibility Equation

PY Percus–Yevick compressibility equation; m constant in Eq. (27); VDW Eq. (27) for $m = 3$; 1 Eq. (28); 2 Eq. (30).
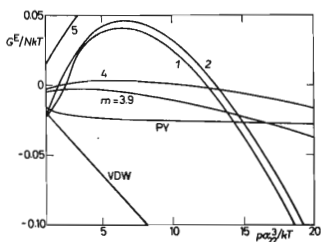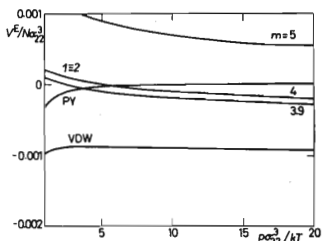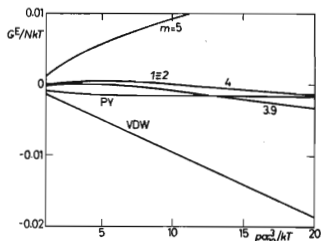

Fig. 2

Pressure Dependence of Excess Gibbs Free Energies of the Equimolar Mixture of Hard Spheres at $h_{11}/h_{22} = 0.4$ and $x_1 = 0.5$ for Different Combination Rules for h_x in the One-Liquid Corresponding States Theory and for the Percus–Yevick Compressibility Equation

For the description cf. Fig. 1.

Fig. 3

Pressure Dependence of Excess Volumes of the Equimolar Mixture of Hard Spheres at $h_{11}/h_{22} = 0.8$ and $x_1 = 0.5$ for Different Combination Rules for h_x in the One-Liquid Corresponding States Theory and for the Percus–Yevick Compressibility Equation

For the description cf. Fig. 1.

Fig. 4

Pressure Dependence of Excess Gibbs Free Energies of the Equimolar Mixture of Hard Spheres at $h_{11}/h_{22} = 0.8$ and $x_1 = 0.5$ for Different Combination Rules for h_x in the One-Liquid Corresponding States Theory and for the Percus–Yevick Compressibility Equation

For the description cf. Fig. 1.

version as it is well known that it is theoretically less plausible than the (p, T) version. By inspection of Table II and Figs 5−8 we find that the optimum value for m in Eq. (31) in the (p, T) version is $m = 5−6$. Eq. (32) yields zero values for both excess functions as is clearly seen from Eqs (26), (33) and (34). This is not far from true because it is definitely known[8] that the values of the excess functions of mixtures of hard spheres at constant pressure are small. Considering the symmetry of the excess functions with respect to x_1, the Percus–Yevick equation in the parameter range covered yields almost symmetrical curves for both G^E and V^E with minima at $x_1 \approx 0.5$. This is true for the one-liquid version only for $m = 3$ and for the two-liquid (p, T) version for $m = 3−4$. However, the differences in the remaining cases are not so striking as to render the general considerations based on the results for $x_1 = 0.5$ invalid. The range for pressures and ratios of hard sphere diameters was chosen so that to cover approximately both the region of existence of liquids and the wide variety in sizes of different molecules encountered in calculations of vapour–liquid equilibria at normal or elevated pressures. Thus we believe that for real molecules the one-liquid version together with Eq. (27) for $m = 4$ and the additional rule for f_x in the form[11]

$$f_x h_x = \sum_{r,s} x_r x_s h_{rs} f_{rs} \qquad (42)$$

Thermodynamic Excess Functions for the Equimolar Binary Mixture of Hard Spheres according to the p, T Version of the Two-Liquid Theory of Corresponding States Expressed by Eq. (26) with the Combination Rules Given by Eqs (31) and (32) at $p\sigma_{22}^3/kT = 12$ and $V_2/N\sigma_{22}^3 = 1.07267$

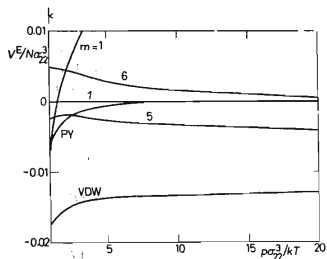| Type of Equation	$h_{11}/h_{22} = 0.4$, $V_1/N\sigma_{11}^3 = 1.36397$		$h_{11}/h_{22} = 0.8$, $V_1/N\sigma_{11}^3 = 1.13026$	
	$V^E/N\sigma_{22}^3$	G^E/NkT	$V^E/N\sigma_{22}^3$	G^E/NkT
Percus–Yevick Eq.	−0.00024	−0.0267	−0.00001	−0.0017
Eq. (31) for $m = 1$	−0.02317	−0.3215	−0.00186	−0.0254
2	−0.01820	−0.2496	−0.00147	−0.0198
3	−0.01324	−0.1781	−0.00108	−0.0142
4	−0.00834	−0.1073	−0.00069	−0.0086
5	−0.00350	−0.0376	−0.00030	−0.0030
6	0.00123	0.0308	0.00009	0.0026
Eq. (32)	0	0	0	0

Fig. 5

Pressure Dependence of Excess Volumes of the Equimolar Mixture of Hard Spheres at $h_{11}/h_{22} = 0.4$ and $x_1 = 0.5$ for Different Combination Rules for h_{xr} in the Two-Liquid Corresponding States Theory and for the Percus–Yevick Compressibility Equation

PY Percus–Yevick compressibility equation; m constant in Eq. (31); VDW Eq. (31) for $m = 3$; 1 Eq. (32). For $m = 1$ the (V, T) version was used; in the remaining cases, the (p, T) version was employed.
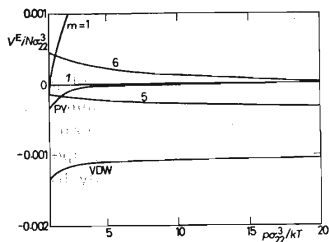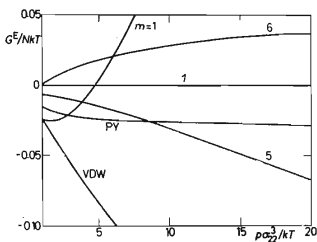

Fig. 6

Pressure Dependence of Excess Gibbs Free Energies of the Equimolar Mixture of Hard Spheres at $h_{11}/h_{22} = 0.4$ and $x_1 = 0.5$ for Different Combination Rules for h_{xr} in the Two-Liquid Corresponding States Theory and for the Percus–Yevick Compressibility Equation

For the description cf. Fig. 5.

Fig. 7

Pressure Dependence of Excess Volumes of the Equimolar Mixture of Hard Spheres at $h_{11}/h_{22} = 0.8$ for and $x_1 = 0.5$ Different Combination Rules for h_{xr} in the Two-Liquid Corresponding States Theory and for the Percus–Yevick Compressibility Equation
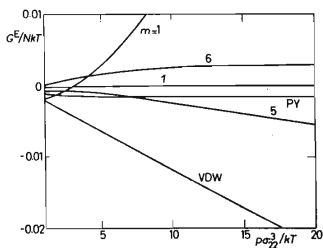
For the description cf. Fig. 5.

Fig. 8

Pressure Dependence of Excess Gibbs Free Energies of the Equimolar Mixture of Hard Spheres at $h_{11}/h_{22} = 0.8$ and $x_1 = 0.5$ for Different Combination Rules for h_{xr} in the Two-Liquid Corresponding States Theory and for the Percus–Yevick Compressibility Equation

For the description cf. Fig. 5.

TABLE III

Thermodynamic Excess Functions for the Equimolar Binary Mixture of Hard Spheres according to the V, T Version of the Two–Liquid Theory of Corresponding States Expressed by Eq. (25) with the Combination Rules Given by Eqs (31) and (32) at $p\sigma_{22}^3/kT = 12$ and $V_2/N\sigma_{22}^3 = 1.07267$

Type of Equation	$h_{11}/h_{22} = 0.4$, $V_1/N\sigma_{11}^3 = 1.36397$		$h_{11}/h_{22} = 0.8$, $V_1/N\sigma_{11}^3 = 1.13026$	
	$V^E/N\sigma_{22}^3$	G^E/NkT	$V^E/N\sigma_{22}^3$	G^E/NkT
Percus–Yevick Eq.	-0.00024	-0.0267	-0.00001	-0.0017
Eq. (31) for $m = 1$	0.02366	0.1434	0.00295	0.0203
2	0.02864	0.2152	0.00334	0.0259
3	0.03360	0.2867	0.00373	0.0315
Eq. (32)	0.14417	1.5405	0.01849	0.1781

or the two-liquid (p, T) version with Eqs (32) or (31) for $m = 5-6$ and

$$f_{xr}h_{xr} = \sum_s x_s f_{rs} h_{rs} \qquad (43)$$

could be successfully used to predict properties of mixtures from those of pure components. The proposed equations could also be applied for the determination of combination rules for constants in empirical equations of state such as for example the recently most successfully used Redlich–Kwong equation in calculating vapour-liquid equilibria at high pressures[13,14]. Further calculations are presently being undertaken.

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