

## MEAN DENSITY APPROXIMATION AND HARD SPHERE EXPANSION THEORY: A REVIEW

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### ABSTRACT

This review surveys research dealing with the Mean Density Approximation (MDA) and the Hard Sphere Expansion (HSE) theory developed by Leland and coworkers. MDA and its modifications provide a simple way to predict radial distribution functions of mixtures from the pure fluid information. Comparisons with computer simulation data show the MDA to be superior to the van der Waals approximation for mixture radial distribution functions. Derivations of the HSE theory and the HSE Conformal Solution Theory (HSE-CST) are also described. For Lennard-Jones mixtures, the HSE theory is proven to be superior to the van der Waals theory by using a proper method to determine the hard-sphere diameter. The major problem associated with the development of a consistent method to determine the hard-sphere diameter of the HSE-CST and the requirements regarding the extension of the HSE-CST to polar mixtures are discussed. It is concluded that the HSE-CST is capable of predicting, satisfactorily, the vapor-liquid equilibrium properties of mixtures containing hydrocarbons and/or slightly quadrupolar or polar compounds such as CO<sub>2</sub> and H<sub>2</sub>S.

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## INTRODUCTION

The radial distribution function (RDF) is proportional to the probability of finding two molecules simultaneously at a given relative separation. The RDF plays a vital role in the theory of fluids, because all the configurational properties of the system can be described in terms of the RDF. For example, If pair-wise additivity of the potential is assumed, compressibility factors of pure fluids and mixtures can be expressed as

$$z = 1 - 2\pi\rho/3kT \int (du/dr) g r^3 dr \quad (1)$$

and

$$z_m = 1 - 2\pi\rho_m/3kT_m \sum \sum x_i x_j \int (du_{ij}/dr) g_{ij} r^3 dr \quad (2)$$

where the subscript m represents the mixture, k is the Boltzmann constant, and g is the RDF. In addition, the RDF of pure fluids can be determined by direct experimental measurements using light or neutron scattering techniques, or by computer simulation with Monte Carlo and molecular dynamics methods. In a mixture, however, the direct experimental measurements are not applicable, which makes computer simulation the only source of this information.

The RDF of a mixture depends upon all the intermolecular parameters and the number densities of every constituent, e.g. in a mixture whose components obey a two parameter potential

$$g_{ij}(r) = f(r, \rho_m, T_m; \{\epsilon_{kl}\}, \{\sigma_{kl}\}, \{x_k\}) \quad (3)$$

Mansoori and Leland (1972) proposed the Mean Density Approximation (MDA) to relate the RDF of a pair in a mixture to that of a hypothetical pure fluid. For spherical molecules, the MDA can be described as

$$g_{ij} = g_o(r/\sigma_{ij}; \rho' \sigma_{ij}^3; kT_m/\epsilon_{ij}), \quad (4)$$

$$\rho' = (\text{mean density}) = \rho_m \sigma_x^3 / \sigma_{ij}^3, \quad (5)$$

Commonly, one assumes the van der Waals relation

$$\sigma_x^3 = \sum \sum x_i x_j \sigma_{ij}^3, \quad (6)$$

In eqns. (4)-(6)  $g_o$  is the RDF of a pure fluid, the subscript x denotes an effective pure fluid value,  $x_i$  is bulk mole fraction of component i in the mixture,  $\sigma$  is the length parameter in the potential function, and  $\epsilon$  is the energy parameter. The composition dependence of this approximation is expressed through the eqn. (6).

Another well known approximation is the van der Waals one-fluid approximation (VDW1), which was introduced by Leland *et al.* (1968) :

$$g_{ij} = g_o(r/\sigma_x; \rho_m \sigma_x^3; kT_m/\epsilon_x) \quad (7)$$

with

$$\sigma_x^3 \epsilon_x = \sum \sum x_i x_j \sigma_{ij}^3 \epsilon_{ij} \quad (8)$$

where the effective length parameter  $\sigma_x$  is defined in eqn. (6). When the  $\epsilon$ -parameters of all pairs are equal, the MDA becomes identical to the VDW1 approximation.

The MDA has many applications: For example, Gonsalves and Leland (1978) used the MDA to modify the regular solution theory; Li *et al.* (1986) incorporated the MDA into the local composition model to evaluate the properties of mixtures. In this communication, we would like to review the progress of recent studies involving the MDA based on computer simulation data, and the Hard Sphere Expansion (HSE) theory, which is one of the important applications of the MDA.

### MEAN DENSITY APPROXIMATION IN HARD-SPHERE MIXTURES

In a hard-sphere mixture the RDF resulting from the MDA theory is identical to the RDF derived from the VDW1 theory. Tan *et al.* (1986) used the RDF resulting from the MDA theory to derive a mixing rule for the hard-sphere diameter,  $d_x$ , from the Ornstein-Zernicke equation,

$$d_x^3 = \sum x_i d_{ii}^3, \quad (9)$$

where  $d_{ii}$  is the hard-sphere diameter of component  $i$ . Eqn. (6) will be identical to this mixing rule only when the following combining rule is used for  $d_{ij}$ .

$$d_{ij}^3 = (d_{ii}^3 + d_{jj}^3)/2 \quad (10)$$

which is in disagreement with the theoretical combining rule for hard-spheres,

$$d_{ij} = (d_{ii} + d_{jj})/2. \quad (11)$$

Prediction of the RDF of a hard-sphere mixture based on the MDA with eqn. (10) as the combining rule seems to be superior to that obtained using eqn. (11) as is demonstrated in Fig. 1 for the contact value of the RDF. One possible explanation of this result is that the approximations in the MDA and the error in eqn. (10) cancel each other and as a result eqn. (10) produces better results than the theoretical eqn. (11).

Tan *et al.* (1986) also observed that the first intersection of the hard-sphere  $g_{ij}$ 's calculated by the MDA and the Monte Carlo simulation always occurs at an intermolecular distance between the first peak and the first minimum of the  $g_{ij}$ 's. Contributions of the deviations between the MDA  $g_{ij}$  values and the simulation  $g_{ij}$  data tend to offset each other in the structural integral,  $I_{ij}$ , calculated as

$$I_{ij}^{(n)} = 4\pi \int y_{ij}^{2-n} g_{ij}(y_{ij}) dy_{ij}; \quad y_{ij} = r_{ij}/d_{ij} \quad (12)$$

because the errors on the two sides of the first  $g_{ij}$  intersection are of opposite sign, as shown in Fig. 1. The structural integrals of the hard-sphere mixture approximated by the MDA, with diameter ratios  $d_{22}/d_{11}=1.5$  to 2.25 and  $x_1=0.2$  to 0.8, were evaluated, and were found to be within 3% deviation from the Monte Carlo simulation data. Obviously, this is the result of the error cancellations in the structural integral calculations, as was pointed out above. (Tan *et al.*, 1986)

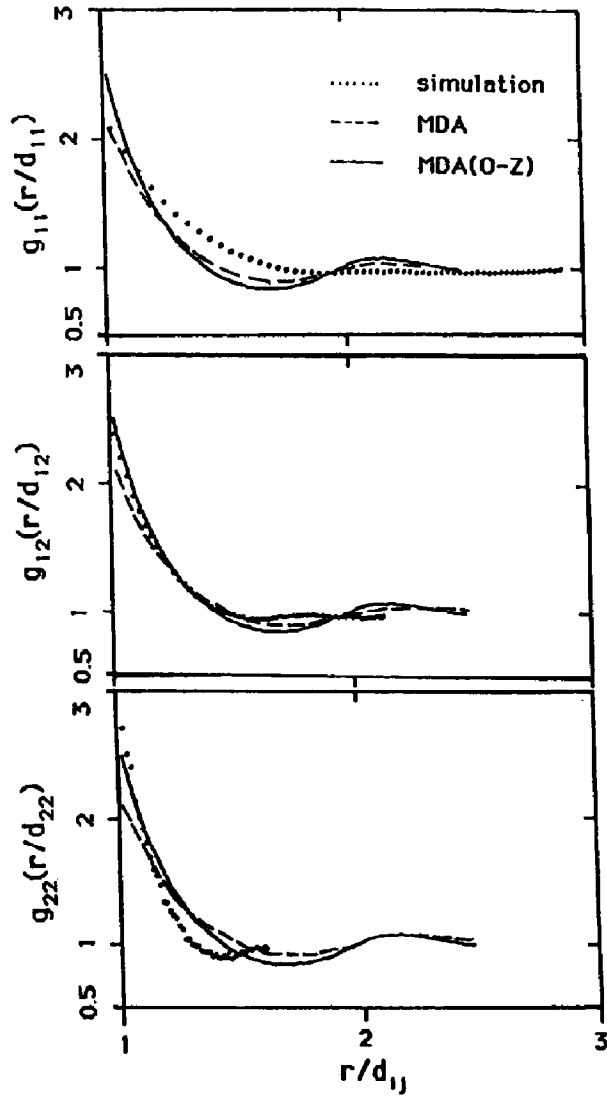


FIGURE 1. RDFs of a binary hard-sphere mixture at  $\rho_m \sum x_i d_{ii} = 0.6$ ,  $x_1 = 0.8$ , and  $d_{22}/d_{11} = 2.0$ . Key: dotted line, Monte Carlo simulation data; solid line, MDA with the combining rule derived from the Ornstein-Zernicke equation [eqn. (10)]; and dashed line, MDA with the conventional combining rule [eqn. (11)] (Tan *et al.*, 1986)

## MEAN DENSITY APPROXIMATION IN LENNARD-JONES MIXTURES

Hoheisel and Lucas (1984) examined the MDA and the VDW1 by molecular dynamics simulation for the binary Lennard-Jones mixtures for the diameter ratio,  $\sigma_{22}/\sigma_{11}$ , varying from 1.0 to 2.0 and with the energy parameter ratio,  $\epsilon_{22}/\epsilon_{11}$ , varying from 0.2 to 5.0 at equimolar composition. They observed that the MDA always gives a better prediction of the  $g_{ij}$ 's than the VDW1 in the region before the second peak. They also showed that the MDA can predict the temperature dependence of the height of the first peak of the  $g_{ij}$ 's better than the VDW1. For structural integrals, their results based on the MDA are generally superior to the results based on the VDW1, particularly at higher orders of exponent  $n$  in eqn. (12). They noted, however, that the predicted structural integrals from both MDA and VDW1 deteriorate as exponent  $n$  or the size ratio increases.

Shukla *et al.* (1986) used the Monte Carlo simulation technique to calculate excess energies of Lennard-Jones mixtures for different size ratios but at large energy parameter ratios,  $\epsilon_{22}/\epsilon_{11} > 2.0$ , and at different compositions. Their results are reported in Table 1 and indicate that the MDA gives good predictions and the VDW1 fails at such high energy parameter ratios (i.e. the MDA gives very good account of the effect of the energy parameter ratio when the size ratio is close to 1.0). They also pointed out that it is quite satisfactory to apply either the MDA or VDW1 for mixtures with size parameter ratios of up to 1.1 and energy parameter ratios of up to 1.5.

For the larger size ratio of  $\sigma_{22}/\sigma_{11} = 2.0$ , Figs. 2 and 3 (Ely, 1986a) indicate that the MDA gives poor predictions of the RDF, especially for the small molecule pair, i.e. the 1-1 pair. Ely (1986a) also pointed out that the MDA consistently underestimates the height of the first peak for the 1-1 pair at such a large size ratio.

## MODIFICATIONS IN THE MEAN DENSITY APPROXIMATION

In order to improve the predictions of mixture RDFs and structural integrals, some efforts have been made to modify the MDA. Hoheisel and Lucas (1984) applied their computer simulation data, empirically, to correlate a scaling function in order to modify structural integrals approximated by the original MDA.

Ely (1986b) used the ratio of the contact values of the the hard-sphere mixture RDFs to scale the RDFs evaluated by the MDA. Such contact value ratios can be analytically calculated using the known hard-sphere equations of state (Carnahan and Starling, 1969; and Mansoori *et al.*, 1971).

Fig. 4 shows that Ely's modification improves RDF prediction for the size ratio of  $\sigma_{22}/\sigma_{11} = 1.07$ . Another advantage of Ely's modification is that it produces improved VDW1 mixing rules. The predicted excess properties for Lennard-Jones mixtures with these improved mixing rules are superior to those calculated with the conventional VDW1 mixing rules, especially for excess volume calculation, as indicated in Fig. 5. In another report, instead of using ratio of hard-sphere contact

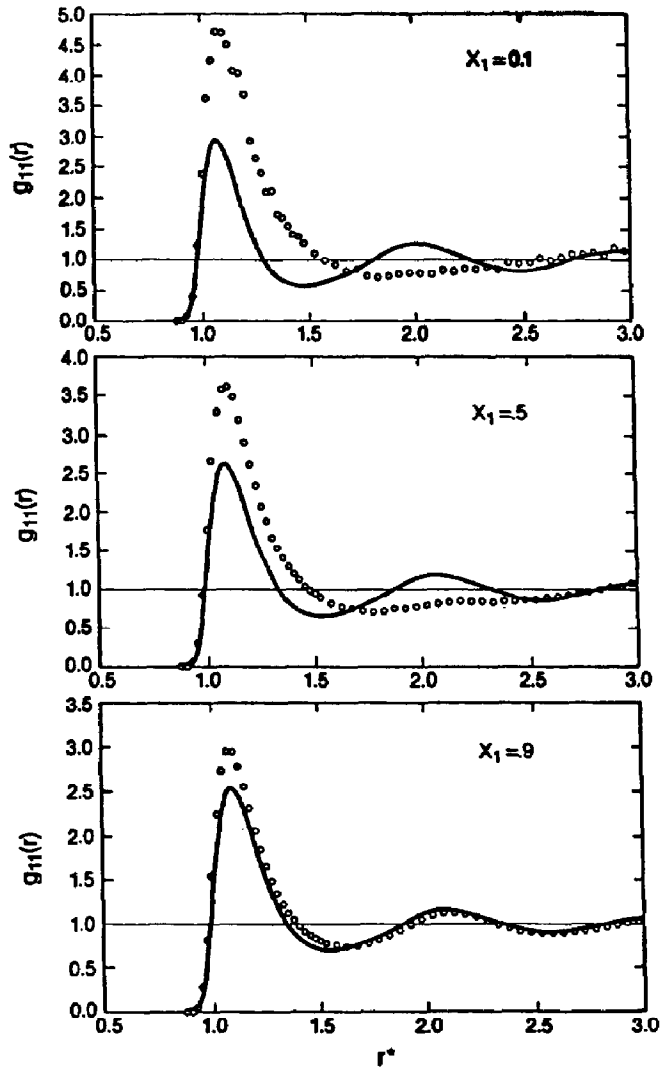


FIGURE 2. Comparison of the MDA (solid line) and simulation results for the 1-1 RDF at three different compositions,  $\epsilon_{22}/\epsilon_{11}=1$  and  $\sigma_{22}/\sigma_{11}=2$ .  $r^*=r/\sigma_{11}$ . (Ely, 1986a)

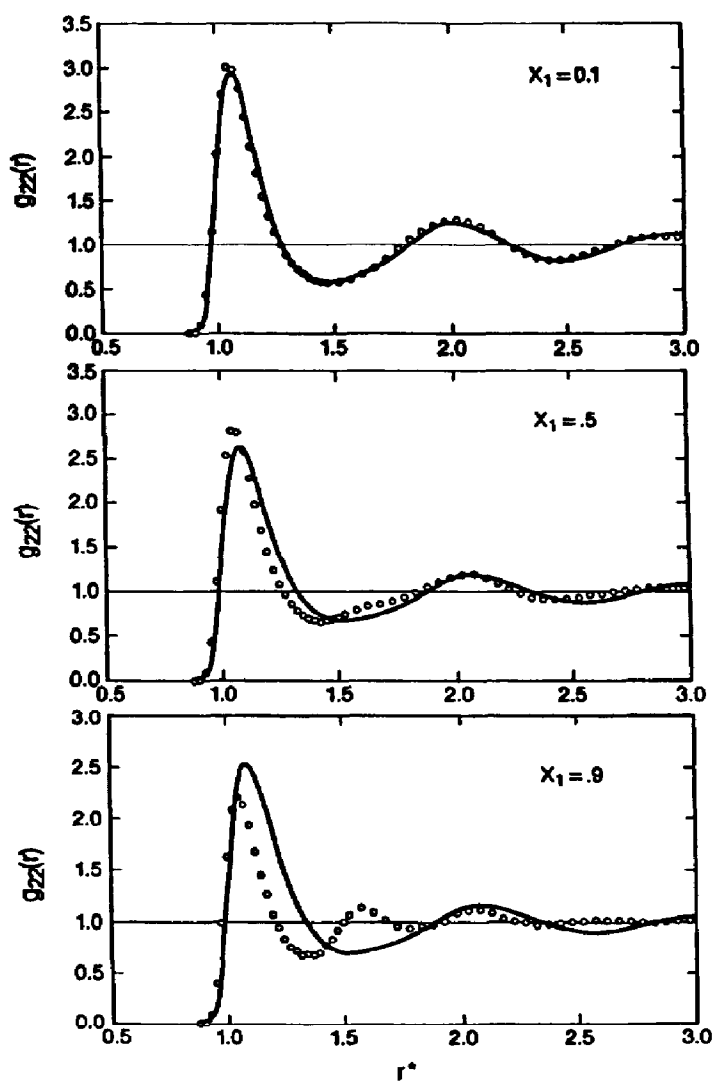


FIGURE 3. Comparison of the MDA (solid line) and simulation results for the 2-2 RDF at three different compositions,  $\epsilon_{22}/\epsilon_{11}=1$  and  $\sigma_{22}/\sigma_{11}=2$ .  $r^*=r/\sigma_{22}$ . (Ely, 1986a)

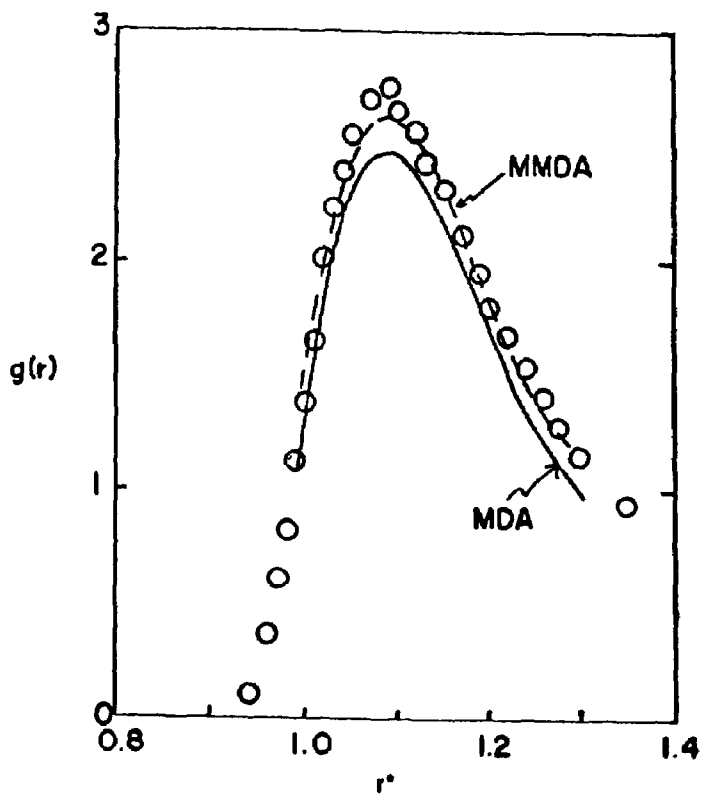


FIGURE 4. Comparison of the predicted RDF for the krypton-krypton pair in an equimolar argon-krypton mixture between the MDA (solid line) and the modified MDA (dashed line). The open circles are computer simulation data.  $r^* = r/\sigma_{kr}$ . (Ely, 1986b)

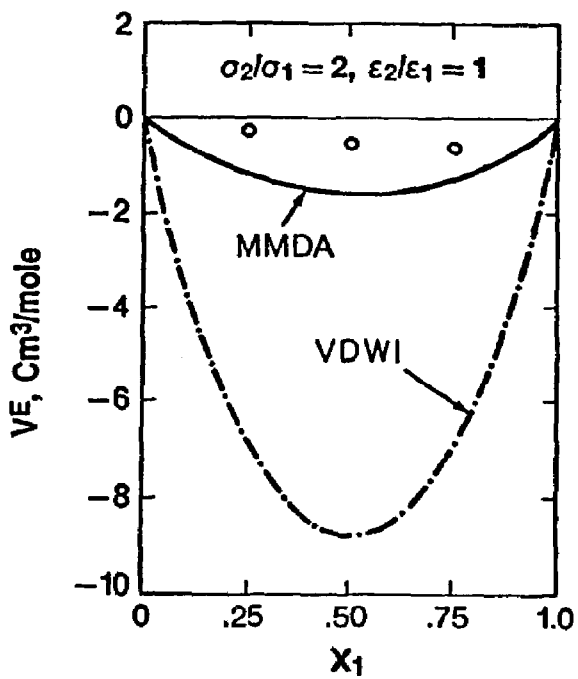


FIGURE 5. Comparison of calculated and simulated (open circles) excess volumes for Lennard-Jones mixtures as a function of composition. (Ely, 1986b)

TABLE 1.

Isochoric excess free energy (J/mol) of some Lennard-Jones mixtures with  $\sigma_{11}=\sigma_{22}=34.05$  nm,  $\rho_m \sigma_x^3=0.75$ , and  $\sigma_x$  given by eqn. (6). (Shukla *et al.*, 1986)

$\epsilon_{11}/k$ [K]	$\epsilon_{22}/k$ [K]	$x_1 = 0.25$			$x_1 = 0.50$			$x_1 = 0.75$		
		MC	VDW1	MDA	MC	VDW1	MDA	MC	VDW1	MDA
T = 120 K										
84.71	169.42	134	154	137	180	207	183	140	156	137
69.17	207.50	335	389	349	444	524	465	348	395	349
59.9	239.6	546	638	566	724	850	754	552	641	665
T = 300 K										
84.71	169.42	125	159	128	166	212	171	125	160	128
69.17	207.50	325	404	327	442	542	436	315	410	327
59.9	239.6	513	653	531	690	876	707	520	664	531

values, Ely (1986a) used the ratio of the first peak of the soft-sphere fluids and applied it for a similar scaling modification. The modifications produced in the latter case also were very encouraging. However, using the hard-sphere contact value (first peak) ratios produces an analytic modification technique.

### DERIVATION OF THE HARD SPHERE EXPANSION (HSE) THEORY

The basic idea behind the HSE theory is the separation of dimensionless properties into repulsive and attractive parts. The strategy starts by dividing the intermolecular potential energy into contributions from repulsive energies, represented by a hard-sphere (HS) potential, spherically symmetrical attractive (sym) energies, and asymmetrical attractive (asym) energies. According to this theory the pair potential can be expressed as

$$u = u^{\text{HS}} + u^{\text{sym}} + u^{\text{asym}}. \quad (13)$$

The symmetrical attraction potential is assumed to be pair-wise additive and in the form (Mansoori and Leland, 1972; Leland, 1976)

$$u^{\text{sym}} = \epsilon f(y), \quad (14)$$

where  $y=r/d$  and  $f(y)$  is a universal function for all components. The analytical expression for the function  $f(y)$  is not required in the HSE theory.

RDFs in a mixture are described by the functional form of the pure reference fluid RDF through the use of the MDA. Expanding the RDFs of the mixture and the reference fluid with respect to hard-sphere RDFs in powers of  $\epsilon/kT$  will produce the following results

$$g_{ij}(y_{ij}, \rho_m d_x^3, \epsilon_{ij}/kT) = g^{\text{HS}}(y_{ij}, \rho_m d_x^3) + (\epsilon_{ij}/kT) \Gamma(y_{ij}, \rho_m d_x^3)$$

$$+ (\epsilon_{ij}/kT)^2 \Psi(y_{ij}, \rho_m d_x^3) + \dots \quad (15)$$

and

$$g(y, \rho_m d_x^3, \epsilon_x/kT) = g^{HS}(y, \rho_m d_x^3) + (\epsilon_x/kT) \Gamma(y, \rho_m d_x^3) \\ + (\epsilon_x/kT)^2 \Psi(y, \rho_m d_x^3) + \dots, \quad (16)$$

where  $\Gamma$  and  $\Psi$  are sums of some complicated integrals (Kirkwood *et al.*, 1952).

For the time being let us neglect the asymmetrical attraction term, and consider it in a later section titled "Extension of the HSE-CST to Polar Mixtures". A perturbation expansion equation of state for the pure reference system in terms of parameters  $\epsilon_x$  and  $d_x^3$  can be obtained by substituting eqns. (13), (14) and (16) into eqn. (1). We may subtract this expanded equation from an analogous expansion for the mixture and obtain

$$z_m - z_r = [ \Sigma \Sigma x_i x_j d_{ij}^3 - d_x^3 ] (2\pi\rho_m/3) \int y^3 (\partial u^{HS}/\partial y) g^{HS} dy \\ + (1/kT) [ \Sigma \Sigma x_i x_j d_{ij}^3 \epsilon_{ij} - d_x^3 \epsilon_x ] (2\pi\rho_m/3) \int y^3 (\partial f/\partial y) g^{HS} dy \\ + (1/kT)^2 [ \Sigma \Sigma x_i x_j d_{ij}^3 \epsilon_{ij}^2 - d_x^3 \epsilon_x^2 ] (2\pi\rho_m/3) \int y^3 (\partial f/\partial y) \Gamma dy \\ + (\text{higher order terms}), \quad (17)$$

where the subscript r denotes a pure reference fluid and m denotes the mixture. The zeroth order term (with respect to  $1/kT$ ), obviously, corresponds to contributions from the hard-sphere fluid. Neglecting the third and higher order terms, pseudo pure fluid potential parameters (pseudo-parameters) for the reference fluid can be evaluated by equating coefficients of  $1/kT$  and  $(1/kT)^2$  terms to zero in eqn. (17),

$$d_x^3 \epsilon_x = \Sigma \Sigma x_i x_j d_{ij}^3 \epsilon_{ij} \quad (18)$$

and

$$d_x^3 \epsilon_x^2 = \Sigma \Sigma x_i x_j d_{ij}^3 \epsilon_{ij}^2. \quad (19)$$

Thus, eqns. (18) and (19) make excess properties of the mixture over the hard-sphere mixture conformal to that of the pure reference. As a result, eqn. (17) can be expressed as

$$z_m(\rho_m, T_m, \{x_i\}) = z_m^{HS}(\rho_m, \{d_i\}, \{x_i\}) + [z_r(\rho_m d_x^3, \epsilon_x/kT) - z_r^{HS}(\rho_m d_x^3)]. \quad (20)$$

Equations of state for the hard-sphere fluid (Carnahan and Starling, 1969) and the hard-sphere fluid mixture (Mansoori *et al.*, 1971) are used to calculate the  $z_r^{HS}$  and  $z_m^{HS}$ , respectively.

## THE HSE THEORY IN LENNARD-JONES MIXTURES

Mansoori and Leland (1972) applied the HSE theory to calculate excess properties of Lennard-Jones mixtures. In addition to two-body interactions, the contributions of the three-body

TABLE 2.  
Excess thermodynamic properties of equimolar Lennard-Jones mixtures at P=0, T=97K,  $\epsilon_{12}/k=133.5$  K,  $\sigma_{12}=35.96$  nm, and  $V^E$  in  $\text{cm}^3/\text{mol}$ . (Chang, 1984)

$\epsilon_{22}/\epsilon_{12}$	Property	MC	VDW1	CO-HSE	VW-HSE
$\sigma_{22}/\sigma_{12}=1.03$					
0.810	$G^E/NkT$	0.242	0.263	0.220	0.240
	$H^E/NkT$	0.240	0.230	0.230	0.250
	$V^E$	-1.080	-1.110	-1.162	-1.010
1.000	$G^E/NkT$	-0.001	-0.003	0.000	0.003
	$H^E/NkT$	0.010	0.000	0.010	0.012
	$V^E$	0.010	-0.051	-0.010	0.000
1.235	$G^E/NkT$	0.112	0.103	0.103	0.099
	$H^E/NkT$	-0.010	0.000	-0.040	-0.060
	$V^E$	-0.800	-0.810	-1.500	-0.650
$\sigma_{22}/\sigma_{12}=1.06$					
0.810	$G^E/NkT$	0.305	0.334	0.280	0.316
	$H^E/NkT$	0.340	0.350	0.280	0.342
	$V^E$	-1.290	-1.390	-1.270	-1.212
1.000	$G^E/NkT$	-0.005	-0.011	0.010	0.010
	$H^E/NkT$	0.030	0.000	0.020	0.043
	$V^E$	0.020	-0.181	-0.011	-0.022
1.235	$G^E/NkT$	0.040	0.014	0.019	0.039
	$H^E/NkT$	-0.100	-0.120	-0.070	-0.067
	$V^E$	-0.680	-0.811	-0.670	-0.550

interactions were also considered. It was assumed that energy contributions of the three-body interactions could be expressed as

$$W = \sum \sum \sum w_{ijk} = \sum \sum \sum (v_{ijk}/d^9) f_2(r_{ij}/d, r_{ik}/d, r_{jk}/d). \quad (21)$$

The superposition approximation was used to calculate the three-body distribution function. By following the same procedure as discussed in the previous section one can derive an additional pseudo-parameter for pure fluid three-body interaction potential as

$$v_x = d_x^3 \sum \sum \sum x_i x_j x_k v_{ijk} / (d_i d_j d_k). \quad (22)$$

In these equations  $d$  represents the hard-sphere diameter. In the case of the Lennard-Jones fluid  $d/\sigma$  is defined as the cut-off parameter. The cut-off parameter was used by Mansoori and Leland (1972) to calculate the hard-sphere diameter, and it was empirically set equal to 0.98. The Barker *et al.*

(1968) perturbation equation was chosen as a reference equation of state. The predicted excess properties (especially the excess volume) from the HSE method were shown to be generally better than the results calculated by the VDW1 method.

Chang *et al.* (1979) used the Verlet-Weis (VW) technique, Verlet and Weis (1972), to calculate the hard-sphere diameter. In that work, the three-body effects were neglected, and reference properties were calculated using the perturbation equation of Weeks *et al.* (1971) in the VW form. Table 2 (Chang *et al.*, 1979) contains excess properties of equimolar Lennard-Jones mixtures calculated by the Monte Carlo simulation technique, the VDW1 method, the HSE theory with cut-off parameter method (CO-HSE), and the HSE theory with VW diameter method (VW-HSE). According to this table, the VW-HSE is better than the VDW1 but slightly worse than the CO-HSE. This table indicates that the HSE method would produce accurate predictions when it is joined with a proper method to determine the effective hard-sphere diameter.

### HSE MIXING RULES

As discussed above, the HSE theory produces mixing rules, given by eqns. (18), (19), and (22) which can be used for calculation of excess properties over the hard-sphere mixture. This should be compared to conventional mixture theories which produce mixing rules for calculation of excess properties over ideal gas mixtures (Mansoori, 1986). A potential disadvantage, however, is that a good representation of the repulsive part of an equation of state is required when HSE mixing rules are applied to calculate mixture properties.

Lan and Mansoori (1976) proposed a perturbation equation of state for pure components by using the Kihara potential as the pair potential and the Axilrod-Teller function for the three-body interaction potential. The hard-sphere equation of Carnahan and Starling (1969) was used for the repulsive term. For mixture calculations, Lan and Mansoori (1977) used the equation of Mansoori *et al.* (1971) to calculate hard-sphere mixture properties. The HSE mixing rules were used. In addition to eqns. (18), (19) and (22), the following equation was also obtained for pseudo-parameter of the Kihara spherical-core diameter,

$$\sigma_x^2 \epsilon_x \zeta_x = \sum \sum x_i x_j \sigma_{ij}^2 \epsilon_{ij} \zeta_{ij}, \quad (23)$$

where  $\zeta$  is the Kihara spherical-core diameter. Excess properties of ten different binary systems and two ternary systems were examined with and without fitting the unlike-pair interaction factor. The results of the HSE mixing rules were shown to be very promising. They also performed a number of vapor-liquid equilibrium calculations. As an example, Table 3 shows bubble temperature calculation of nitrogen-argon-oxygen ternary system, where the binary interaction parameters were obtained from fitting to binary data.

Dimitrelis and Prausnitz (1986) applied the HSE method to a two-parameter equation of state in which the Carnahan-Starling equation was used for its repulsive term. They performed several vapor-liquid equilibrium calculations for nonpolar mixtures and showed that the HSE method was

TABLE 3.

Bubble temperature calculation of nitrogen(1)-argon(2)-oxygen(3) mixtures. Subscripts L and V represent liquid and vapor phase, respectively. (Lan and Mansoori, 1977)

$X_{1,L}$	$X_{2,L}$	$T^{EXP}(K)$	$T^{HSE}(K)$	$X_{1,v}^{EXP}$	$X_{1,v}^{HSE}$	$X_{2,v}^{EXP}$	$X_{2,v}^{HSE}$
P = 6.08 bar							
0.890	0.024	97.6	95.2	0.950	0.950	0.012	0.012
0.771	0.062	98.7	96.4	0.884	0.889	0.074	0.032
0.515	0.188	101.5	99.5	0.707	0.722	0.074	0.111
0.364	0.181	103.7	100.5	0.570	0.589	0.091	0.121
0.229	0.174	105.9	104.3	0.412	0.430	0.127	0.133
P = 18.24 bar							
0.762	0.184	116.5	116.1	0.839	0.840	0.126	0.125
0.597	0.097	119.3	119.0	0.708	0.702	0.074	0.071
0.262	0.094	124.8	124.7	0.380	0.388	0.091	0.080
0.110	0.119	127.6	128.1	0.181	0.183	0.127	0.112
0.017	0.107	129.8	130.5	0.030	0.030	0.122	0.108

consistently better than the VDW1 method, especially for system with large molecular size differences.

### HARD SPHERE EXPANSION CONFORMAL SOLUTION THEORY (HSE-CST)

This theory was proposed by Chang *et al.* (1979) to make the HSE theory applicable to real systems (see also Chen, 1982a; Chen *et al.*, 1982b; and Hang and Leland 1986). The objectives were to avoid using empirical mixing rules for equations of state and to furnish a better composition dependence to the thermodynamic properties of real systems. Fig. 6 schematically shows the procedure which should be followed in constructing a HSE-CST method based on an empirical equation of state.

In the HSE-CST method, the symmetrical attraction potential is defined, as in eqn. (14), to be a two-parameter function. The conformal parameters  $f_{ij}$  and  $h_{ij}$  are introduced to account for the nonconformality for real fluids. Thus,

$$f_{ij} = \epsilon_{ij}/\epsilon_{rr} \quad (24)$$

and

$$h_{ij} = (d_{ij}/d_{rr})^3, \quad (25)$$

where the subscript r represents the reference fluid. The pseudo-parameters are derived by substituting eqns. (24) and (25) into eqns. (18) and (19) giving

$$f_x h_x = \Sigma \Sigma x_i x_j f_{ij} h_{ij} \quad (26)$$

and

$$f_x^2 h_x = \sum \sum x_i x_j f_{ij}^2 h_{ij} \quad (27)$$

The shape factors,  $\theta_{ir}$  and  $\phi_{ir}$ , proposed by Leach *et al.* (1968) are used to relate the conformal parameters to critical properties :

$$f_{ir} = \theta_{ir} T_{ci} / T_{cr} \quad (28)$$

$$h_{ir} = \phi_{ir} V_{ci} / V_{cr} \quad (29)$$

and for the pseudo-parameters it is assumed that

$$f_x = T_{cm} / T_{cr} \quad (30)$$

and

$$h_x = V_{cm} / V_{cr} \quad (31)$$

where the subscript c represents a critical property, and the subscript m denotes the mixture. Expressions for the pseudo-critical properties are derived by substituting eqns. (28) - (31) into eqns. (26) and (27), where the cross terms are related to the pure fluid properties by the combining rules:

$$\epsilon_{ij} = \xi_{ij} \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad (32)$$

and

$$d_{ij}^3 = \lambda_{ij} (d_{ii}^3 + d_{jj}^3) / 2, \quad (33)$$

where  $\xi_{ij}$  and  $\lambda_{ij}$  are the energy and volume unlike-pair factors, respectively. These factors are empirically adjusted to fit the experimental data of the binary mixture. Instead of using the theoretical combining rule for the hard-sphere diameter, eqn. (33) is applied as the combining rule as proposed by Tan *et al.* (1986). The resulting pseudo-critical properties of the HSE-CST for the mixture are in the form,

$$T_{cm} = \frac{\sum \sum x_i x_j (\theta_{ir} T_{ci} \theta_{jr} T_{cj}) \xi_{ij}^2 \lambda_{ij} (\phi_{ir} V_{ci} + \phi_{jr} V_{cj}) / 2}{\sum \sum x_i x_j (\theta_{ir} T_{ci} \theta_{jr} T_{cj})^{1/2} \xi_{ij} \lambda_{ij} (\phi_{ir} V_{ci} + \phi_{jr} V_{cj}) / 2} \quad (34)$$

and

$$V_{cm} = \frac{\{ \sum \sum x_i x_j (\theta_{ir} T_{ci} \theta_{jr} T_{cj})^{1/2} \xi_{ij} \lambda_{ij} (\phi_{ir} V_{ci} + \phi_{jr} V_{cj}) \}^2}{\sum \sum x_i x_j (\theta_{ir} T_{ci} \theta_{jr} T_{cj}) \xi_{ij}^2 \lambda_{ij} (\phi_{ir} V_{ci} + \phi_{jr} V_{cj}) / 2} \quad (35)$$

In this conformal solution technique, the symmetrical attraction contributions of the nonpolar reference fluid are assumed to be conformal to those of the mixture with these pseudo-critical parameters, i.e. the mixture excess properties can be calculated from the reference fluid at the same reduced condition as the mixture. The reference properties are evaluated at the conditions

$$T_r = (T_m / T_{cm}) T_{cr} = T_m / f_x \quad (36)$$

and

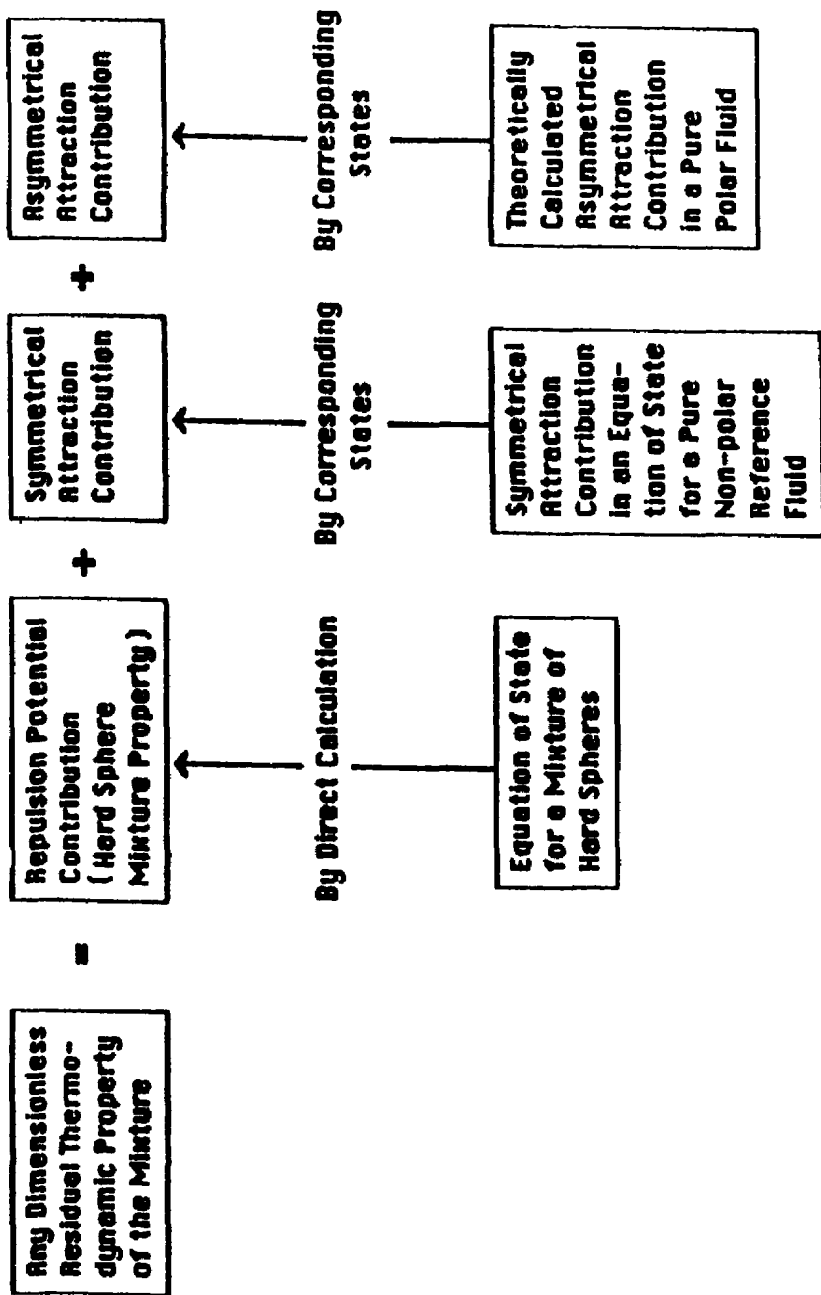


FIGURE 6. The HSE conformal solution procedures for mixture properties calculations. (Chen *et al.*, 1982b)

$$\rho_r = \rho_m V_{cm}/V_{cr} = \rho_m h_x \quad (37)$$

The equivalent condition for component i in the mixture is defined as

$$T_i = (T_m/T_{cm})T_{ci}\theta_{ir} = T_r f_{ir} \quad (38)$$

and

$$\rho_i = \rho_m V_{cm}/V_{ci}\phi_{ir} = \rho_r/h_{ir} \quad (39)$$

Eqn. (20) can be written as

$$z_m(\rho_m, T_m, \{x_i\}) = z_m^{HS}(\rho_m, \{d_i\}, \{x_i\}) + [z_r^{ES}(\rho_r, T_r) - z_r^{HS}(\rho_r, d_r^3)] \quad (40)$$

where the superscript ES represents the property calculated by an empirical equation of state. Once a systematic way to determine the effective hard-sphere diameter  $d_r$  for the reference fluid is available, the diameter for each constituent in the mixture can be evaluated from eqns. (25) and (39), viz,

$$d_i^3 = \rho_r d_r^3 / \rho_i \quad (41)$$

Thus, in order to utilize the HSE-CST method for thermodynamic property calculation of real fluid mixtures one needs to know the effective hard-sphere diameter of the reference fluid. This subject is discussed in the next section.

## EFFECTIVE HARD-SPHERE DIAMETER FOR FLUIDS WITH UNKNOWN POTENTIAL, HSE-CST MIXTURES CALCULATIONS

A review paper by Smith (1973) has summarized and compared different formulations for the determination of the hard-sphere diameter using the perturbation and variational techniques. Among such formulations, the VW diameter method and the cut-off parameter method, mentioned earlier, can be used to determine the effective hard-sphere diameter for fluids whose intermolecular potentials are known. However, the direct application to real fluids of the other formulations reviewed by Smith is ambiguous because of the lack of knowledge concerning potential functions between real molecules. For such fluids, the HSE-CST attempts to determine the effective hard-sphere diameter from thermodynamic properties calculated from an empirical equation of state.

According to Chang *et al.* (1979) one approach to determine effective diameters is the following: Any empirical equation of state for the compressibility factor can be expressed conceptually as

$$z = z_1^+(\rho) + z_2^+(\rho, T) + z^-(\rho, T) \quad (42)$$

where the superscripts + and - represent repulsive and attractive contributions, respectively. When eqn. (42) is generated by a potential with a hard-core, similar to the Kihara potential, the  $z_1^+$  would represent the contribution of the hard-core and  $z_2^+$  would represent the soft repulsion. Since the attractive forces are of long range, they only have minor effects at very high densities. Bienkowski and Chao (1975) proposed the high density limit approach to determine the hard-core volume from

TABLE 4.  
Prediction of compressibility factors of methane-propane mixtures by the HSE-CST method with  $\xi_{ij}=0.965$ . (Chen, 1982a)

T(K)	P(bar)	$x_{\text{methane}}$	z(EXPT.)	z(HSE)	Dev.(%)
344	13.9	0.7	0.9606	0.9609	0.03
344	137.9	0.7	0.7089	0.6917	-2.43
344	689.5	0.7	1.5172	1.4984	-1.24
444	13.9	0.7	0.9847	0.9841	-0.06
444	137.9	0.7	0.9079	0.9050	-0.32
444	689.5	0.7	1.4157	1.4120	-0.26
444	41.3	0.5	0.9232	0.9275	0.47
444	137.9	0.5	0.8289	0.8199	-1.09
444	413.7	0.5	1.0850	1.0804	-0.42
478	86.2	0.1	0.7605	0.7535	-0.92
478	275.8	0.1	0.8671	0.8694	0.27
478	689.5	0.1	1.6128	1.6163	0.22

Average absolute deviation = 0.65 %

TABLE 5.  
Prediction of vapor-liquid equilibrium constants of methane-propane mixtures by the HSE-CST method with  $\xi_{ij}=0.965$  and T=294 K. (Chen, 1982a)

P(bar)	$K_{C1}^{EXP}$	$K_{C1}^{HSE}$	Dev(%)	$K_{C3}^{EXP}$	$K_{C3}^{HSE}$	Dev(%)
10.3	14.27	13.77	-3.45	0.8578	0.8599	0.24
13.8	10.70	10.52	-1.64	0.6787	0.6885	1.44
24.1	6.10	6.10	0.00	0.4587	0.4675	1.92
31.0	4.74	4.74	0.00	0.4055	0.4077	0.54
34.5	4.25	4.27	0.45	0.3895	0.3888	-0.18
41.3	3.54	3.55	0.14	0.3696	0.3654	-1.14
48.2	3.00	3.02	0.74	0.3519	0.3554	0.99
55.1	2.601	2.606	0.18	0.3694	0.3563	-3.55
68.9	2.022	1.977	-2.23	0.3977	0.3894	-2.09
75.9	1.804	1.710	-5.21	0.4228	0.4213	-0.35
82.8	1.617	1.602	-0.92	0.4527	0.4693	3.67
89.7	1.442	1.450	0.55	0.5128	0.5421	5.71
96.6	1.209	1.207	-0.13	0.6813	0.7454	9.40

Average absolute deviation for  $K_{C1}^{HSE} = 1.20$  % and for  $K_{C3}^{HSE} = 2.40$  %

the isothermal compressibility. Applying the high density limit to eqn. (42), we obtain

$$\lim_{\rho \rightarrow \infty} z \approx \lim_{\rho \rightarrow \infty} [z_1^+(\rho) + z_2^+(\rho, T)]. \quad (43)$$

Also, since empirical equation of state formulations are usually fitted in powers of the reciprocal temperature, the other limiting case, the high temperature limit yields

TABLE 6.

Prediction of vapor-liquid equilibrium constants of ethane-n-butane-n-pentane mixtures by the HSE-CST method at T=394 K.  $C=x_{c4}/(x_{c4}+x_{c5})$ . (Chen and Chen, 1985)

P(bar)	C	$K_{C2}^{EXP}$	$K_{C2}^{HSE}$	$K_{C4}^{EXP}$	$K_{C4}^{HSE}$	$K_{C5}^{EXP}$	$K_{C5}^{HSE}$
37.9	0.2	2.161	2.166	0.757	0.752	0.475	0.477
51.7	0.2	1.575	1.577	0.737	0.720	0.535	0.514
64.8	0.2	1.148	1.111	0.874	0.900	0.805	0.823
31.0	0.4	2.570	2.553	0.816	0.818	0.503	0.513
44.8	0.4	1.780	1.772	0.744	0.733	0.518	0.500
62.0	0.4	1.150	1.117	0.878	0.899	0.806	0.817
31.0	0.6	2.550	2.448	0.825	0.831	0.512	0.529
44.8	0.6	1.719	1.707	0.753	0.750	0.548	0.525
58.0	0.6	1.155	1.129	0.877	0.907	0.847	0.822
31.0	0.8	2.480	2.355	0.836	0.842	0.525	0.548
41.3	0.8	1.839	1.773	0.777	0.774	0.555	0.542
51.1	0.8	1.400	1.357	0.812	0.812	0.688	0.656
53.8	0.8	1.220	1.108	0.905	0.932	0.816	0.865

Average absolute deviation for  $K_{C2}^{HSE} = 2.72\%$ , for  $K_{C4}^{HSE} = 1.44\%$ ,  
and for  $K_{C5}^{HSE} = 3.17\%$ .

$$\lim_{T \rightarrow \infty} z = z_1^+(\rho). \quad (44)$$

In the HSE-CST, the  $z^{HS}$  term accounts for all the repulsion effects, i.e. we can write

$$z^{HS} = z_1^+(\rho) + z_2^+(\rho, T). \quad (45)$$

Since eqn. (43) overestimates the repulsion contribution, the optimal hard-sphere property will fall between the two limiting cases. These limits become nearly upper and lower bounds for the optimal repulsion contribution. Based on this, Chang *et al.* (1979) proposed the quadratic fitting method to calculate the optimal hard-sphere properties by considering a limited temperature range along an isochore at a given density. Several calculations of bulk phase thermodynamic properties for mixtures were satisfactorily carried out by Chang *et al.* (1979). Unfortunately, however, Chang's method failed to predict the vapor-liquid equilibrium constants, presumably due to errors in their effective hard-sphere diameters.

Chen *et al.* (1982b) developed the characteristic temperature method for determining the effective hard-sphere diameter. In this method, a property is expanded about the temperature at the inflection point of the isochore. As a result, all the mixture properties, even the vapor-liquid equilibrium constants, could be predicted successfully, as shown in Tables 4 and 5. However the low temperature results, where the isochores are straight, were poor. The feasibility of the HSE-CST method in multicomponent mixture calculations was examined by Chen and Chen (1985). Satisfactory results were obtained in ternary and five-component systems, as shown in Tables 6 and 7. In the case of multicomponent calculations, all the unlike-pair interaction parameters were

TABLE 7.

Prediction of vapor-liquid equilibrium constants of methane-ethane-propane-n-butane-n-pentane mixtures by the HSE-CST method at T=311 K. (Chen and Chen, 1985)

P (bar)	Expt.					HSE-CST				
	$K_{C1}$	$K_{C2}$	$K_{C3}$	$K_{C4}$	$K_{C5}$	$K_{C1}$	$K_{C2}$	$K_{C3}$	$K_{C4}$	$K_{C5}$
35.7	5.678	1.514	0.407	0.175	0.059	5.388	1.386	0.432	0.169	0.072
65.3	2.981	0.873	0.368	0.122	0.089	3.047	0.968	0.368	0.167	0.080
89.5	2.231	0.813	0.393	0.190	0.093	2.220	0.872	0.392	0.201	0.105
98.7	2.010	0.872	0.419	0.196	0.124	2.070	0.872	0.421	0.226	0.122

Average absolute deviation for  $K_{C1}^{HSE} = 3.05\%$ , for  $K_{C2}^{HSE} = 6.06\%$ ,  
 for  $K_{C3}^{HSE} = 2.38\%$ , for  $K_{C4}^{HSE} = 13.38\%$ ,  
 and for  $K_{C5}^{HSE} = 11.42\%$ .

TABLE 8.

Prediction of vapor-liquid equilibrium constants of methane-ethane mixtures by the HSE-CST method with  $\xi_{ij}=0.982$  and T=158 K.

P(bar)	$K_{C1}^{EXP}$	$K_{C1}^{HSE}$	Dev(%)	$K_{C2}^{EXP}$	$K_{C2}^{HSE}$	Dev(%)
1.78	8.25	8.60	4.29	0.113	0.115	1.52
2.76	5.70	5.60	-1.70	0.0773	0.0782	1.10
4.82	3.27	3.21	-1.93	0.0504	0.0506	0.39
9.66	1.51	1.51	-0.13	0.0392	0.0396	0.96
13.72	1.061	1.058	-0.24	0.0438	0.0519	18.55

Average absolute deviation for  $K_{C1}^{HSE} = 1.66\%$  and for  $K_{C2}^{HSE} = 4.51\%$ .

determined by fitting to binary experimental data. The unlike-pair factors were found to be independent of temperature. These results indicate that the HSE-CST has very good composition dependence, allowing constant unlike-pair interaction factors to be used over a wide range of density and temperature.

Hang and Leland (1986) applied the variational inequality minimization theory of Mansoori (1983) and Alem and Mansoori (1984) to obtain a more sophisticated method to calculate the effective hard-sphere diameter at high densities. In addition, a second order variational principle was proposed by them, for the medium to low density region, by modifying the characteristic temperature method. Good results for vapor-liquid equilibrium calculations were obtained for hydrocarbon systems, even in the low temperature region, as summarized in Table 8.

Finally, we note that in the HSE-CST method, all molecules are assumed to be spherical, which is obviously an approximation. As expected, the HSE-CST predictions deteriorate when the mixture contains long chain molecules. Naumann and Leland (1984) and Kwon (1986) have

successfully proposed the Hard Convex-Body Expansion (HCBE) theory to overcome this problem.

## EXTENSION OF THE HSE-CST TO POLAR MIXTURES

The HSE approach can be easily extended to systems which exhibit asymmetrical terms in the attractive potential. Neglecting anisotropic overlap forces, the asymmetrical pair potential would then consist of contributions due to electrostatic, induction, and dispersion forces. Mathematically,

$$u^{\text{asym}} = u^{\text{el}} + u^{\text{ind}} + u^{\text{disp}}. \quad (46)$$

By applying the spherical harmonic expansion method to eqn. (46), an expression for the asymmetrical contribution to the Helmholtz free energy,  $A^{\text{asym}}$ , has been derived in thermodynamic perturbation theory (Larsen *et al.*, 1977; Gubbins and Twu, 1978; and Moser *et al.*, 1981). The general form of  $A^{\text{asym}}$  is given as

$$A^{\text{asym}} = A_2^{\text{el}} + A_2^{\text{ind}} + A_2^{\text{disp}} + A_2^{\text{el,ind}} + A_2^{\text{el,disp}} + A_2^{\text{ind,disp}} + A_3^{\text{el}} + \dots \quad (47)$$

where subscripts 2 and 3 indicate contributions from 2-body and 3-body interaction forces, respectively. Among these contributions, the electrostatic terms, which arise from interactions between permanent multipole moments, are dominant. In the HSE-CST method proposed by Hang and Leland (1986), only the electrostatic contributions are considered in the calculation of asymmetrical effects, while Induction and dispersion effects are considered to be small and accounted for through shape factors. A Pade' approximation for the  $A^{\text{asym}}$  is applied by using  $A_2^{\text{el}}$  and  $A_3^{\text{el}}$  in the form,

$$A^{\text{asym}} = A_2^{\text{el}} / [ 1 - (A_3^{\text{el}}/A_2^{\text{el}}) ]. \quad (48)$$

Stell *et al.* (1974) have shown that results obtained from eqn. (48) are in good agreement with the computer simulation results. They also suggested, since the thermodynamic properties are most accurately obtained from the Helmholtz free energy using the Pade' approximation, that eqn. (48) should be used to derive other properties. For example, the asymmetrical attraction contribution of the compressibility factor can be calculated by

$$z^{\text{asym}} = 1 + (\rho/kT)(\partial A^{\text{asym}}/\partial \rho)_T. \quad (49)$$

For a pure fluid, Larsen *et al.* (1977) and Moser *et al.* (1981) have derived expressions for the second order term  $A_2$  and the 2-body and 3-body third order terms  $A_{3,2}$  and  $A_{3,3}$ . They found

$$\begin{aligned} A_2/RT = & -\rho/(kT)^2 [ 1/6 (\mu^4/d^3)I_{\text{HS}}^{(6)} + 1/2 (\mu^2Q^2/d^5)I_{\text{HS}}^{(8)} \\ & + 7/10 (Q^4/d^7)I_{\text{HS}}^{(10)} + 8/5 (\mu^2\Omega^2/d^7)I_{\text{HS}}^{(10)} \\ & + 36/5 (Q^2\Omega^2/d^9)I_{\text{HS}}^{(12)} + 4752/175 (\Omega^4/d^{11})I_{\text{HS}}^{(14)} \end{aligned} \quad (50)$$

$$\begin{aligned} A_{3,2}/RT = & \rho/(kT)^3 [ 2/5 (\mu^4Q^2/d^8)I_{\text{HS}}^{(11)} + 12/35 (\mu^2Q^4/d^{10})I_{\text{HS}}^{(13)} \\ & + 36/245 (Q^6/d^{12})I_{\text{HS}}^{(15)} ] \end{aligned} \quad (51)$$

$$A_{3,3}/RT = \rho^2/(kT)^3 [1/54 (\mu^6/d^3)I_{HS}^{DDD} + 1/480 (\mu^4Q^2/d^5)I_{HS}^{DDQ} + 1/640 (\mu^2Q^4/d^7)I_{HS}^{DQQ} + 1/6400 (Q^6/d^9)I_{HS}^{QQQ}] \quad (52)$$

and

$$A_3 = A_{3,2} + A_{3,3} \quad (53)$$

where  $\mu$ ,  $Q$ , and  $\Omega$  are dipole, quadrupole, and octopole moments, respectively. In equations (47)-(49) the 2-body and 3-body structural integrals are defined as

$$I_{HS}^{(n)} = 4\pi \int y^{2-n} g_{HS}(y) dy \quad (54)$$

and

$$I_{HS}^{triple} = \int w(y_1, y_2, y_3) g_{HS}^{(3)}(y_1, y_2, y_3) dy_1 dy_2, \quad (55)$$

where  $y_1 = \rho_{ij}/d$ ,  $y_2 = \rho_{ik}/d$ ,  $y_3 = \rho_{jk}/d$ ,  $w$  is the 3-body interaction potential, and  $g_{HS}^{(3)}$  is the triplet distribution function of the hard-sphere fluid. Larsen *et al.* (1977) have correlated all structural integrals for hard-sphere fluids resulting from computer simulation data in polynomial form.

For HSE-CST mixture calculations of Hang and Leland (1986), structural integrals in eqns. (50)-(52) are replaced by the mixture structural integrals,  $I_{HSM}^{(n)}$ . Then the MDA is applied to approximate  $I_{HSM}^{(n)}$  by the  $I_{HS}^{(n)}$  of a pure reference fluid according to

$$I_{HSM}^{(n)} = I_{HS}^{(n)}(\rho_m d_x^3) \quad (56)$$

and

$$I_{HSM}^{triple} = I_{HS}^{triple}(\rho_m d_x^3) \quad (57)$$

and the multipoles in eqns. (50)-(52) are replaced by the following pseudo-parameters:

For 2-body interaction contributions in the second order term:

$$(\mu^4)_x = d_x^3 \sum \sum x_i x_j (\mu_i^2 \mu_j^2 / d_{ij}^3), \quad (58)$$

$$(\mu^2 Q^2)_x = d_x^5 \sum \sum x_i x_j (\mu_i^2 Q_j^2 / d_{ij}^5), \quad (59)$$

$$(Q^4)_x = d_x^7 \sum \sum x_i x_j (Q_i^2 Q_j^2 / d_{ij}^7), \quad (60)$$

$$(\mu^2 \Omega^2)_x = d_x^7 \sum \sum x_i x_j (\mu_i^2 \Omega_j^2 / d_{ij}^7), \quad (61)$$

$$(Q^2 \Omega^2)_x = d_x^9 \sum \sum x_i x_j (Q_i^2 \Omega_j^2 / d_{ij}^9), \quad (62)$$

and

$$(\Omega^4)_x = d_x^{11} \sum \sum x_i x_j (\Omega_i^2 \Omega_j^2 / d_{ij}^{11}). \quad (63)$$

For 2-body interaction contributions in the third order term:

$$(\mu^4 Q^2)_{x,2} = d_x^8 \sum \sum x_i x_j (\mu_i^2 \mu_j^2 Q_i Q_j / d_{ij}^8), \quad (64)$$

$$(\mu^2 Q^4)_{x,2} = d_x^{10} \Sigma \Sigma x_i x_j (\mu_i^2 Q_i Q_j^3 / d_{ij}^{10}), \quad (65)$$

and

$$(Q^6)_{x,2} = d_x^{12} \Sigma \Sigma x_i x_j (Q_i^3 Q_j^3 / d_{ij}^{12}). \quad (66)$$

Finally, for 3-body interaction contributions in the third order term:

$$(\mu^6)_{x,3} = d_x^3 \Sigma \Sigma \Sigma x_i x_j x_k (\mu_i^2 \mu_j^2 \mu_k^2 / d_{ij} d_{ik} d_{jk}), \quad (67)$$

$$(\mu^4 Q^2)_{x,3} = d_x^5 \Sigma \Sigma \Sigma x_i x_j x_k (\mu_i^2 \mu_j^2 Q_k^2 / d_{ij} d_{ik}^2 d_{jk}^2), \quad (68)$$

$$(\mu^2 Q^4)_{x,3} = d_x^7 \Sigma \Sigma \Sigma x_i x_j x_k (\mu_i^2 Q_j^2 Q_k^2 / d_{ij}^2 d_{ik}^2 d_{jk}^3), \quad (69)$$

and

$$(Q^6)_{x,3} = d_x^9 \Sigma \Sigma \Sigma x_i x_j x_k (Q_i^2 Q_j^2 Q_k^2 / d_{ij}^3 d_{ik}^3 d_{jk}^3). \quad (70)$$

In the HSE-CST calculation of Hang and Leland (1985) the unlike-pair diameter,  $d_{ij}$ , is defined by eqn. (33), and  $d_x$  is defined by eqn. (6). After including the asymmetrical attraction effects in the HSE-CST method, eqn. (40) becomes

$$z_m(\rho_m, T_m, \{x_i\}) = z_m^{HS}(\rho_m, \{d_i\}, \{x_i\}) + [z_r^{ES}(\rho_r, T_r) - z_r^{HS}(\rho_m, d_r^3)] \\ + z_r^{asym}(\rho_m, T_m, (\mu^4)_x, (\mu^2 Q^2)_x, \dots). \quad (71)$$

This equation extends the HSE-CST method to polar mixtures.

Hang and Leland (1985) made a comparison of the K-value calculations for  $C_2H_6-H_2S$  and  $CO_2-C_3H_8$  systems between two computational methods:

- (i) One method is the direct computation of polar effects by means of the Pade' approximant (as mentioned earlier in this section). Shape factors are then used only for residual nonpolar, nonconformality with the reference, i.e. shape factors are determined by the equations :

$$z_r - z_r^{asym} = z_i - z_i^{asym} \quad (72)$$

and

$$(A-A*)_r / RT_r - (A-A*)_r^{asym} / RT_r = (A-A*)_i / RT_i - (A-A*)_i^{asym} / RT_i. \quad (73)$$

- (ii) The other method is to use shape factors only to account for both polar and nonpolar types of nonconformality, i.e. shape factors are calculated by simultaneously solving the equations,

$$z_r = z_i \quad (74)$$

and

$$(A-A*)_r / RT_r = (A-A*)_i / RT_i. \quad (75)$$

The first method had some advantages over the second method for the  $C_2H_6-H_2S$  system, especially at low temperatures. Hydrogen sulfide, according to its structure, possesses dipole, quadrupole, and higher moments, but only the dipole moment is available from experimental data.

When a fitted quadrupole moment was used for  $\text{H}_2\text{S}$ , the results were significantly improved. However, the two methods were comparable for the  $\text{CO}_2\text{-C}_3\text{H}_8$  system. In order to confirm the advantages of one method over another, more varieties of mixtures with wider temperature and density ranges should be examined.

## CONCLUSIONS

The MDA gives an excellent approximation of structural integrals for hard-sphere mixtures with diameter ratios less than 2.25 when using the combining rule derived from the Ornstein-Zernicke equation. This conclusion supports the soundness of the theoretical structure of the HSE theory. The MDA was also applied successfully in the HCBE for real fluid mixtures consisting of long-chain molecules. Comparisons of computer simulation data for long-chain molecules with the MDA+HCBE might reveal the reasons for the success of this theory.

For Lennard-Jones mixtures, the MDA provides a satisfactory approximation for small size-difference systems and furnishes very good energy parameter ratio dependence. It is promising to develop modifications of the MDA which are capable of improving the conventional mixing rules. The HSE theory is shown to be superior to the VDW1 theory in predicting Lennard-Jones mixture properties when the hard-sphere diameters are properly determined. Furthermore, the HSE-CST method supplies accurate predictions for systems containing light hydrocarbons, and polar and quadrupolar compounds such as  $\text{H}_2\text{S}$  and  $\text{CO}_2$ . It will be challenging to extend the HSE-CST (or HCBE theory) to mixtures containing also highly polar (hydrogen bonding) and/or quantum fluids.

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## NOMENCLATURE

A	Helmholtz free energy
d	Hard-sphere diameter
f	A universal function for the symmetrical attraction potential
$f_{ij}$	Energy conformal parameter defined in eqn. (24)
g	Radial distribution function
$h_{ij}$	Volume conformal parameter defined in eqn. (25)
I	Structural integrals defined in eqn. (12)
k	Boltzmann constant
Q	Permanent quadrupole moment

R	Gas constant
r	Distance
T	Temperature
u	Pair potential energy function
V	Volume
W	Total 3-body interaction potential
w	3-body interaction potential
x	Mole fraction
y	Dimensionless distance defined in eqn. (12)
z	Compressibility factor

### Greek Letters

$\sigma$	Length parameter of a pair potential
$\epsilon$	Energy parameter of a pair potential
$\theta_{ir}$	Energy shape factor of component i with respect to component r
$\lambda_{ij}$	Unlike pair interaction coefficient defined in eqn. (33)
$\mu$	Permanent dipole moment
$\nu$	3-body interaction parameter
$\zeta$	Kihara hard-core diameter
$\xi_{ij}$	Unlike pair interaction coefficient defined in eqn. (32)
$\rho$	Density
$\phi_{ir}$	Volume shape factor of component i with respect to component r
$\Omega$	Permanent octopole moment

### Superscripts

asym	Asymmetrically attractive contribution
DDD	Triple dipole interaction
DDQ	Dipole-dipole-quadrupole interaction
disp	Dispersion contribution
DQQ	Dipole-quadrupole-quadrupole interaction
el	Electrostatic contribution
ES	Property calculated from an equation of state
HS	Hard-sphere property
ind	Induction contribution

n	Order of the structural integral defined in eqn. (12)
QQQ	Triple quadrupole interaction
sym	Symmetrically attractive contribution
+	Repulsive contribution
-	Attractive contribution
*	Property of an ideal gas state of a fluid at same temperature and density as the actual fluid
'	Pseudo-parameter used for the mean density defined in eqn. (5)

### Subscripts

c	Critical property
HS	Hard-sphere fluid
i	Component i
j	Component j
m	Mixture
o	Pure fluid
r	Reference fluid
x	Pseudo-parameter for hypothetical pure reference fluid

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