STATISTICAL MECHANICAL MODELING OF ASSOCIATING SOLUTIONS

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ABSTRACT

One major obstacle in the development of statistical mechanical models for associating fluids and fluid mixtures has been the lack of accurate intermolecular potential models for such systems. One theory which has shown to be promising in solving this problem without the need for intermolecular potential function is the fluctuation theory of mixtures. This paper consists of recent work of the authors on the development of a new fluctuation theory approaches for calculation of total, partial molar properties, and phase equilibria of associating fluid mixtures. This technique is based upon the newly developed exact relations among the mixture direct correlation function integrals and the closures for unlike-interaction direct correlation function integrals. A new closure for unlike-interaction direct correlation function integrals is suggested and the effect of pressure on the coefficients of two closures is studied.

INTRODUCTION

Associating solutions are characterized by the formation of aggregates of similar or dissimilar molecules in solution. This behavior creates difficulties in trying to deal with such solutions by the usual methods. A promising method for dealing with associating solutions is the utilization of the pair correlation function, g_{ij}. This function gives the total correlation between a pair of molecules i and j as a function of the distance between them. The physical significance of the pair correlation function can be seen by considering a solution of total

volume V and number of molecules of type i, N_i. The number of molecules of type j in a spherical shell of thickness dr and a distance r from a central i molecule is given by $\rho_j \, g_{ij} \, 4\pi r^2$ dr where $\rho_j = N_j / V$. It is clear that this quantity increases with an increase in association strength.

In a mixture of n components there are $n(n-1)/2$ pair correlation functions. The link between these functions and solution properties is provided by integrals over the spacial coordinates of the pair correlation functions. These integrals are known as the fluctuation integrals. The knowledge of the fluctuation integrals and their relations in mixtures is important in the development of mixture theories of complex molecules. Studies on concentration fluctuations in mixtures have resulted in numerous advances in the fundamental understanding of behavior of mixtures at, and away from, equilibrium (Gibbs, 1948; Landau and Lifshitz, 1980). The engineering concept of "local compositions" can be linked to the statistical mechanical theory of concentration fluctuations (Mansoori and Ely 1985).

Among the concentration fluctuation theories of statistical mechanics the Kirkwood-Buff solution theory is the one which is developed specifically for mixtures at equilibrium (Kirkwood and Buff, 1951). Obtaining thermodynamic properties from this theory requires knowledge of the fluctuation integrals, G_{ij}.

$$G_{ij} \quad \int_0^\infty [g_{ij}(r) - 1] 4\pi r^2 dr \tag{1}$$

The solution thermodynamic properties can also be expressed in terms of integrals of the direct correlation functions C_{ij}:

$$C_{ij} = \int_0^\infty c_{ij}(r) 4\pi r^2 dr \tag{2}$$

where $c_{ij}(r)$ is the direct correlation function defined in terms of $g_{ij}(r)$ as follows (Ornstenin and Zernike, 1914; Pearson and Rushbrooke, 1957):

$$c_{ij}(r_{12}) = g_{ij}(r_{12}) - \sum_{k=1}^{n} \rho_k \int c_{ik}(r_{13})[g_{ij}(r_{23}) - 1] dr_3 \tag{3}$$

Evaluating these integrals from microscopic information such as the intermolecular potential energy has not been easy. This is because our knowledge about the intermolecular potential energy functions of real fluids is incomplete and the present techniques for calculating these integrals from potential energy functions are very lengthy and tedious. New and exact relations between direct correlation function integrals are reported in a previous publication (Hamad 1988, Hamad and Mansoori 1990a, b). Also, since the direct correlation function integrals have simple shapes and short ranges we report here the use of simple combining

rule (closure), between unlike and like interaction direct correlation integrals, which in turn lead to information about G_{ij}'s.

THEORY OF CALCULATING C_{ij}'S

In what follows we present the technique for calculating C_{ij}'s and G_{ij}'s for multicomponent mixtures. To derive the relations among the C_{ij} integrals we use the mathematical fact that the mixed second derivatives of a function of two or more variables are equal at all points where the derivatives are continuous.

Let us consider a system which is described by the following set of independent variables $(T, \rho_1, \rho_2, ..., \rho_n)$, where T is the absolute temperature, $\rho_i = N_i/V$, N_i is the number of molecules i in the system, V is the system volume, and n is the number of components in the mixture. In the grand canonical ensemble the following expression for $\partial \mu \rho_i / \partial \rho_i$ is derived (O'Connell 1971; Landau and Lifshitz 1980).

$$(\partial \mu_i / \partial \rho_i)\, T,\ \rho_j{}' = kT\{\delta_{ij}/\rho_i - C_{ij}\} \tag{4}$$

where $\rho_j{}'$ stands for the set $\rho_1, \rho_2, ..., \rho_n$ variables excluding ρ_j

$$\tilde{\sigma}_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases} \tag{5}$$

Using Eq. (4) exact relations can be derived among the direct correlation function integrals, C_{ij}, by differentiating this equation with respect to ρ_i and equating the mixed second derivatives of the chemical potentials (Hamad and Mansoori 1990a). For example, for a binary mixture with T, ρ_1, ρ_2 as the independent variables one can write:

$$\partial C_{12} / \partial \rho_1 = \partial C_{11} / \partial \rho_2 \tag{6}$$

and

$$\partial C_{12} / \partial \rho_2 = \partial C_{22} / \partial \rho_1 \tag{7}$$

The above two equations are exact relating C_{11}, C_{22}, and C_{12}. In order to solve these equations for C_{11}, C_{22} and C_{12} one needs a closure relation among C_{11}, C_{22} and C_{12} to get the three direct correlation function integrals. In the next section a number of closure expressions for C_{12} are considered.

CHOICE OF THE C_{12} CLOSURE

Simultaneous solution of Eqs. (6) and (7) for C_{11}, C_{22} and C_{12} is not possible without another expression relating C_{12} to C_{11} and C_{22} so that

$$C_{12} = C_{12}(C_{11}, C_{22}; T, \rho_1, \rho_2, \ldots, \rho_n) \tag{8}$$

We choose to call Eq. (8), the C_{12} closure. The exact C_{12} closure expression is not presently available. There exist variety of ways of assuming the closure for the direct correlation function integrals. With an appropriate choice for the functional form of the closure expression, Eqs. (6, 7, 8), can be solved simultaneously for C_{11}, C_{22} and C_{12}. Then the fluctuation integrals G_{11}, G_{22} and G_{12} can be derived from C_{11}, C_{22} and C_{12} using the following equations (Pearson and Rushbrooke 1957; O'Connell 1971).

$$\rho G_{ii} = \frac{\rho C_{ii} - (1-x_i)\rho^2(C_{11}C_{22} - C_{12}^2)}{1 - x_1\rho C_{11} - x_2\rho C_{22} + x_1 x_2 \rho^2(C_{11}C_{22} - C_{12}^2)} \tag{9}$$

$$\rho G_{12} = \frac{\rho C_{12}}{1 - x_1\rho C_{11} - x_2\rho C_{22} + x_1 x_2 \rho^2(C_{11}C_{22} - C_{12}^2)} \tag{10}$$

Two expressions for the closure have been suggested: the geometric mean (Hamad and Mansoori, 1990a):

$$C_{12} = (C_{11}C_{22})^{1/2} \tag{11}$$

and the weighted arithmetic mean (Hamad and Mansoori, 1990b):

$$C_{12} = \alpha_{21}C_{11} + \alpha_{12}C_{22} \tag{12}$$

The geometric mean gives very accurate predictions for mixtures of hard spheres at high densities, and the arithmetic mean gives a good representation of associating liquid mixtures at ambient pressure. The activity coefficient expressions derived from Eq. (12) were used to predict accurately vapor-liquid and liquid-liquid phase equilibria of associating liquids at ambient pressures (Hamad and Mansoori, 1990b). To extend the applicability of this model to higher pressures, the effect of pressure on the coefficients α_{21} and α_{12} need to be known. In this work a new closure expression is suggested and the effect of pressure on the closure coefficients is studied.

A NEW CLOSURE EXPRESSION

A source of information about the mathematical form of the C_{ij} closure is based on the fact that the virial expansion of the direct correlation function integral can be written in the following form (Hamad 1988).

$$C_{ij} = -(2B^{(2)}_{ij} + 3\sum_{k=1}^{n} B^{(3}_{ijk}\rho_k + 4\sum_{k=1}^{n}\sum_{ll=1}^{n} B^{(4)}_{ijkl}\rho_k\rho_l + ...)$$ (13)

where $B^{(2)}_{ij}$, $B^{(3)}_{ijk}$ and $B^{(4)}_{ijkl}$ are the second, third and fourth virial coefficients, respectively. From this equation one concludes that $C_{ij} = -2 B_{ij}^{(2)}$ where $B^{(2)}_{ij}$ (T) is the second virial coefficient of the pair i and j at low densities.

The second virial coefficient can be written in the following form:

$$B_{ij}^{(2)} = \sigma_{ij}^3 f_{ij}(T)$$ (14)

where σ_{ij} is the size parameter and f_{ij} is a temperature function. The unlike size parameter σ_{ij} (i $\neq$ j) can be expressed in terms of σ_{ii} as:

$$\sigma_{ij} = \sigma_{ii}/2 + \sigma_{jj}/2$$ (15)

In the limit of low density Eqs. (14, 15) give the following relation between C_{ij}:

$$C_{ij} = \frac{1}{2}[\frac{f_{ij}}{f_{ii}}]^{1/3}C_{ii}^{1/3} + \frac{1}{2}[\frac{f_{ij}}{f_{jj}}]^{1/3}C_{jj}^{1/3}$$ (16)

A relation similar to this one is suggested at higher densities and is written as follows:

$$C_{ij}^{1/3} = \alpha_{ji} C_{ii}^{1/3} + \alpha_{ij} C_{jj}^{1/3}$$ (17)

At low densities the coefficients α_{ji} and α_{ij} are independent of pressure, and their behavior at liquid densities is studied later in this work.

TEST OF THE SUGGESTED CLOSURE

The validity of Eq. (17) at high densities can be tested by comparison to experimental data. A simple way to make the comparison is to divide Eq. (17) by $C_{ii}^{1/3}$. This gives a linear relation between $(C_{ij}/C_{ii})^{1/3}$ and $(C_{jj}/C_{ii})^{1/3}$. For binary mixtures one has:

$$(C_{12}/C_{11})^{1/3} = \alpha_{21} + \alpha_{12}(C_{22}/C_{11})^{1/3} \tag{18}$$

The experimental values of C_{ij} needed to test the above equation were obtained from experimental G_{ij} values (Matteoli and Lepori, 1984) by utilizing the following relations for binary mixtures:

$$\rho C_{ii} = \frac{\rho G_{ii} - (1-x_i)\rho^2(G_{11}G_{22} - G_{12}^2)}{1 - x_1\rho G_{11} - x_2\rho G_{22} + x_1 x_2\rho^2(G_{11}G_2 - G_{12}^2)} \tag{19}$$

$$\rho C_{12} = \frac{\rho G_{12}}{1 - x_1\rho G_{11} - x_2\rho G_{22} + x_1 x_2\rho^2(G_{11}G_{22} - G_{12}^2)} \tag{20}$$

Figure 1 shows the results of the linearity test for the liquid mixtures of water-methanol and water-aminoethanol. The linearity is very clear and this supports the suggested closure. The new closure is also compared to Eq. (12) which was suggested before (Hamad and Mansoori, 1990a) and the results are reported in Table 1. The two closures give about the same average absolute derivations which are fairly small. Actual C_{ij} values are shown in Figures 2-4.
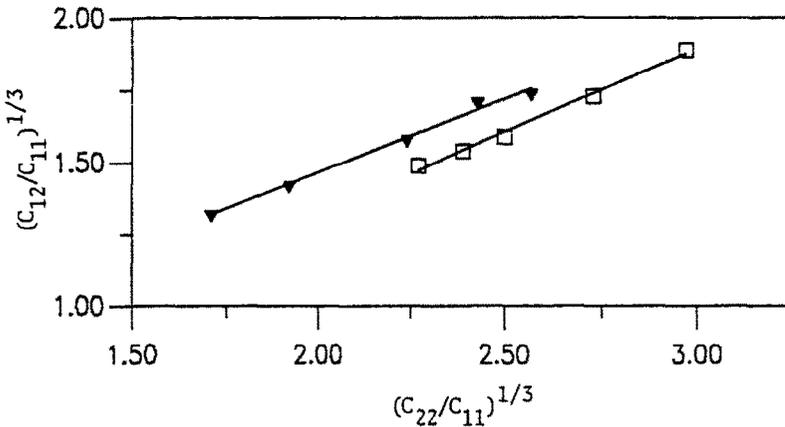

Figure 1.   Linearity test for $(C_{22}/C_{11})^{1/3}$ versus $(C_{12}/C_{11})^{1/3}$ for Water (1) + Methanol (2) (▾) and Water (1) + aminoethanol (2) (☐).

TABLE 1

Deviation of the predicted C_{12}/C_{11} from experimental values

System	Eq. 12		%AAD[a]	Eq. 17		%AAD
	α_{21}	α_{12}		α_{21}	α_{12}	
Water-methanol	1.033	0.2602	2.1	0.4466	0.5093	1.9
Water-aminoethanol	0.3908	0.2395	1.9	0.1630	0.5774	2.1
Water-ethanol	1.5646	0.1794	5.4	0.5603	0.4318	5.3
TCM[b]-methanol	0.4251	-0.0204	2.5	0.7518	-0.0042	2.5
TCM-ethanol	0.6549	-0.0150	0.76	0.8681	-0.0030	0.92
TCM-propanol	0.7917	0.0140	0.62	0.9227	0.0063	0.66
TCM-1-butanol	0.9539	0.0200	0.53	0.9766	0.0140	0.53
TCM-Dioxane	0.3412	0.7066	0.58	0.3749	0.6386	0.58

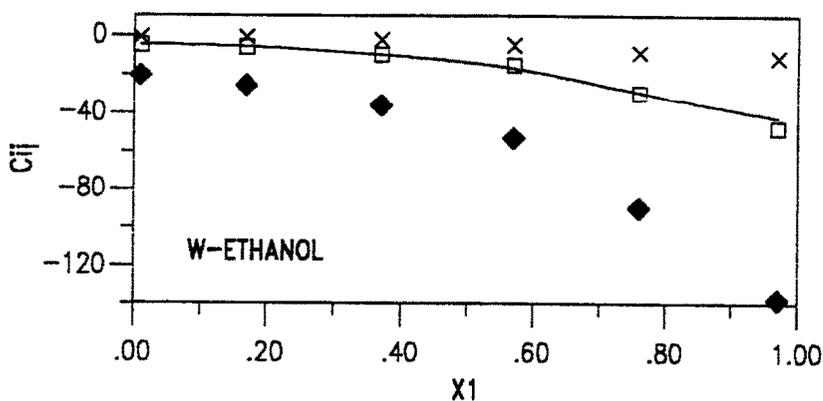a: %AAD = $1/n \Sigma |$(exp. - pred.)/exp. $|$;   b: TCM stands for tetrachloromethane

Figure 2: The variation of ρC_{ij} with composition for water (1) + Methanol (2) at 298 K. ρC_{11} (*); ρC_{12} ($\square$) and ρC_{22} ($\blacklozenge$). The solid curve represents the ρC_{12} predicted by the present theory.
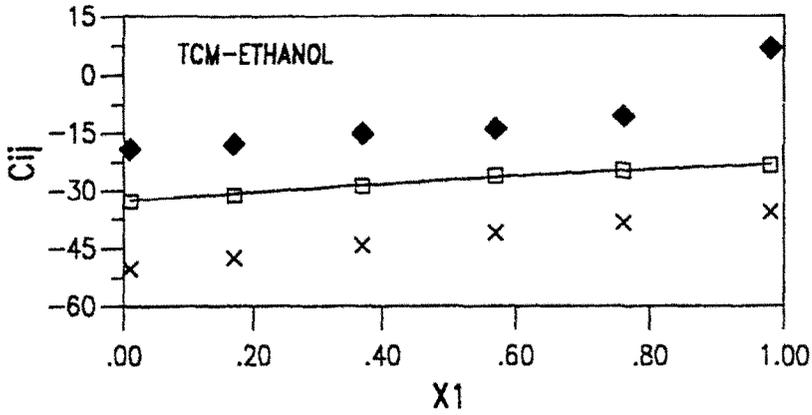
Figure 3: The variation of ρC_{ij} with composition for tetrachloromethane (1) + Ethanol (2) at 298K. ρC_{11} (*); ρC_{12} (□) and ρC_{22} (♦). The solid curve represents the ρC_{12} predicted by the present theory.
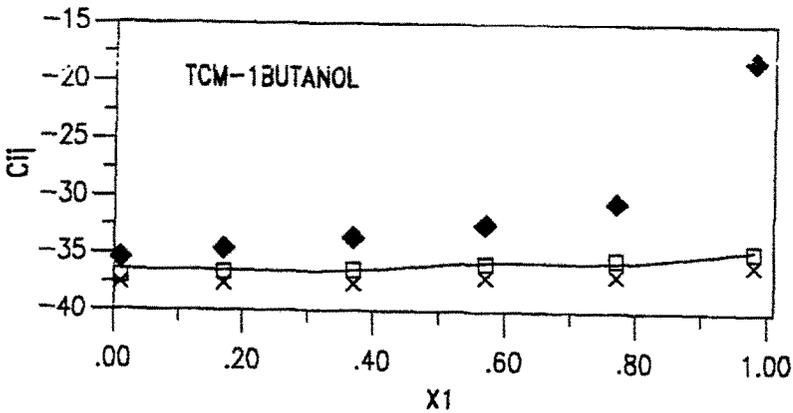

Figure 4: The variation of ρC_{ij} with composition for tetrachloromethane (1) + 1-Butanol (2) at 298K. ρC_{11} (*); ρC_{12} (□) and ρC_{22} (♦). The solid curve represents the ρC_{12} predicted by the present theory.

DEPENDENCE OF THE CLOSURE COEFFICIENTS ON PRESSURE

Knowledge about the dependence of the coefficients of Eqs. (12) and (17) on pressure is important in utilizing these equations for liquids at high pressures. These coefficients will vary with pressure because they are related to the volumes, isothermal compressibilities and the derivatives $\partial \ln \gamma_i / \partial x_i$ of pure components and at infinite dilution. However, the variation with pressure is unknown because the above quantities are unknown in general.

To find the effect of pressure on the coefficients α_{21} and α_{12} one needs experimental values C_{ij}'s at high pressures, but they are not available in the literature and the same is true for G_{ij} values. However, the derivatives $(\partial G_{ij} / \partial P)_{x, T}$ are reported in the mixtures. These derogates can be used to get a good approximation for G_{ij}'s at high pressure by writing.

$$G_{ij}\ (P_2) = G_{ij}\ (P_1) + \ (P_2 - P_1) \partial G_{ij} / \partial P \tag{21}$$

provided that P_2 and P_1 are not very far apart. The values of G_{ij} at $P_1 = 1$ bar are available in the literature (Matteoli and Lepori 1984, Lepori and Matteoli 1988) which allows the calculation of G_{ij} at higher pressures. The values of C_{ij}'s can then be calculated from Eqs. (19, 20) and the results used to find the coefficients α_{21} and α_{12}. This procedure was followed in finding the coefficients reported in Table 2. The table shows that α_{ij} can

TABLE: 2

Effect of Pressure on Closure Coefficients

System	Pressure (bar)	Eq. 12		Eq. 17	
		α_{21}	α_{12}	α_{21}	α_{12}
Water - Ethanol	1	1.157	0.127	0.681	0.308
"	100	0.729	0.171	0.415	0.423
"	1000	-0.049	0.300	-0.066	0.659
TCM[a] - Ethanol	1	0.631	-0.019	0.857	0.0033
"	100	0.686	-0.131	0.871	-0.019
"	1000	0.756	-0.061	0.909	-0.017
TCM - 1Butanol	1	1.143	-0.171	1.133	-0.143
"	100	1.118	-0.124	1.093	-0.095
"	1000	1.187	0.013	1.056	0.009

a TCM stands for Tetrachloromethane

either increase or decrease with pressure, and in most cases a monotonic behavior is observed. In such cases an exponential function seems to represent the dependence of the coefficients on pressure fairly well. Further study in this area is needed to come up with more general statements regarding the effect of pressure on the closure coefficients.

CONCLUSIONS:

It is possible to predict the direct correlation functions based on simple closure expressions. In this paper a new closure is suggested and tested using experimental data. The closure compares well with the behavior of experimental data. The coefficients of the suggested closure and of the weighted arithematic mean shows mostly a monotonic variation with pressure.

ACKNOWLEDGMENTS

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