

## 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,  $G_{ij}$ .

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

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

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

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

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

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 ( $T, \rho_1, \rho_2, \dots, \rho_n$ ), 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  $\partial\mu_i/\partial\rho_i$  is derived (O'Connell 1971; Landau and Lifshitz 1980).

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

where  $\rho_j'$  stands for the set  $\rho_1, \rho_2, \dots, \rho_n$  variables excluding  $\rho_j$

$$\delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases} \quad (5)$$

Using Eq. (4) exact relations can be derived among the direct correlation function integrals,  $C_{ij}$ , by differentiating this equation with respect to  $\rho_i$  and equating the mixed second derivatives of the chemical potentials (Hamad and Mansoori 1990a). For example, for a binary mixture with  $T, \rho_1, \rho_2$  as the independent variables one can write:

$$\partial C_{12}/\partial\rho_1 = \partial C_{11}/\partial\rho_2 \quad (6)$$

and

$$\partial C_{12}/\partial\rho_2 = \partial C_{22}/\partial\rho_1 \quad (7)$$

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

$$C_{12} = C_{12}(C_{11}, C_{22}, T, \rho_1, \rho_2, \dots, \rho_n) \quad (8)$$

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).

$$\rho G_{11} = \frac{\rho C_{11} - (1-x_1)\rho^2(C_{11}C_{22} - C_{12}^2)}{1-x_1\rho C_{11} - x_2\rho C_{22} + x_1x_2\rho^2(C_{11}C_{22} - C_{12}^2)} \quad (9)$$

$$\rho G_{12} = \frac{\rho C_{12}}{1-x_1\rho C_{11} - x_2\rho C_{22} + x_1x_2\rho^2(C_{11}C_{22} - C_{12}^2)} \quad (10)$$

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

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

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

$$C_{12} = \alpha_{21} C_{11} + \alpha_{12} C_{22} \quad (12)$$

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  $\alpha_{21}$  and  $\alpha_{12}$  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).

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

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:

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

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

$$\sigma_{ij} = \sigma_{ii}^{1/2} + \sigma_{jj}^{1/2} \quad (15)$$

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

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

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

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

At low densities the coefficients  $\alpha_{ji}$  and  $\alpha_{ij}$  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:

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

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:

$$\rho C_{ii} = \frac{\rho G_{ii} - (1-x_i)\rho^2(G_{11}G_{22} - G_{12}^2)}{1-x_i\rho G_{11} - x_i\rho G_{22} + x_i x_j \rho^2(G_{11}G_{22} - G_{12}^2)} \quad (19)$$

$$\rho C_{12} = \frac{\rho G_{12}}{1-x_i\rho G_{11} - x_j\rho G_{22} + x_i x_j \rho^2(G_{11}G_{22} - G_{12}^2)} \quad (20)$$

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.

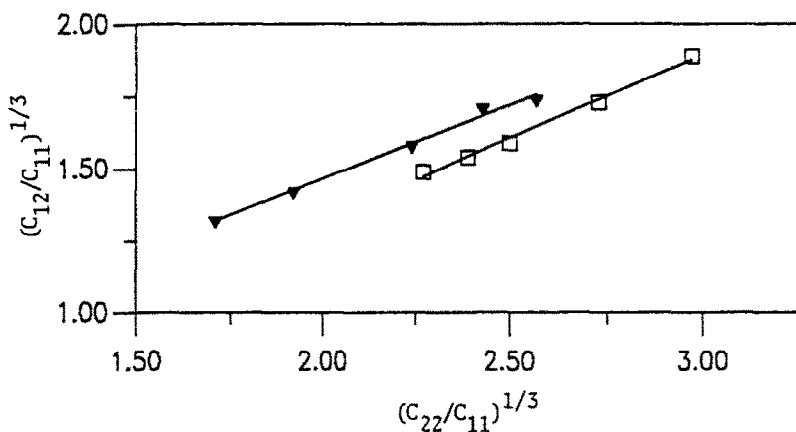


Figure 1. Linearity test for  $(C_{22}/C_{11})^{1/3}$  versus  $(C_{12}/C_{11})^{1/3}$  for Water (1) + Methanol (2) (▼) and Water (1) + aminoethanol (2) (□).

TABLE 1

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

System	Eq. 12		%AAD <sup>a</sup>	Eq. 17		%AAD
	$\alpha_{21}$	$\alpha_{12}$		$\alpha_{21}$	$\alpha_{12}$	
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 <sup>b</sup> -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 =  $1/n \sum |(exp. - pred.) / exp. |$ ; b: TCM stands for tetrachloromethane

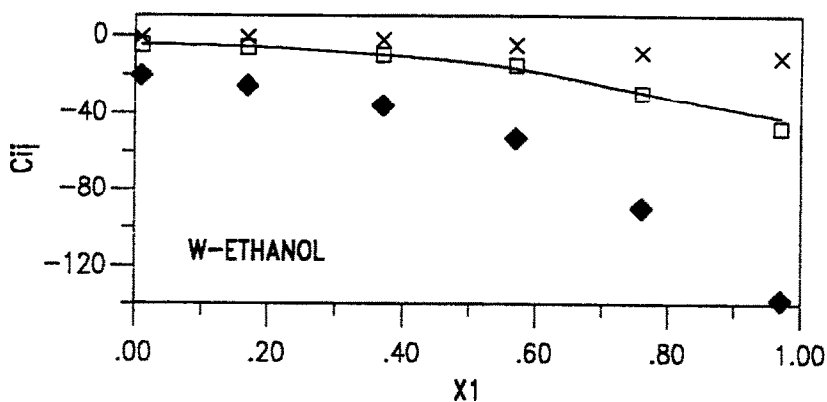


Figure 2: The variation of  $\rho C_{ij}$  with composition for water (1) + Methanol (2) at 298 K.  $\rho C_{11}$  (\*);  $\rho C_{12}$  (□) and  $\rho C_{22}$  (♦). The solid curve represents the  $\rho C_{12}$  predicted by the present theory.

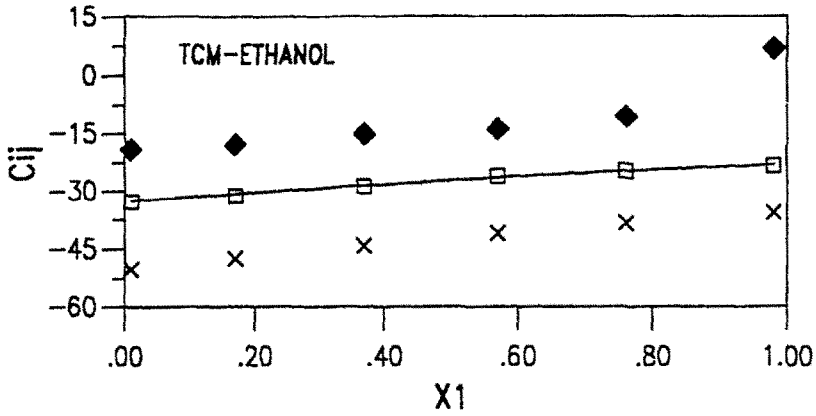


Figure 3: The variation of  $\rho C_{ij}$  with composition for tetrachloromethane (1) + Ethanol (2) at 298K.  $\rho C_{11}$  (\*);  $\rho C_{12}$  (□) and  $\rho C_{22}$  (♦). The solid curve represents the  $\rho C_{12}$  predicted by the present theory.

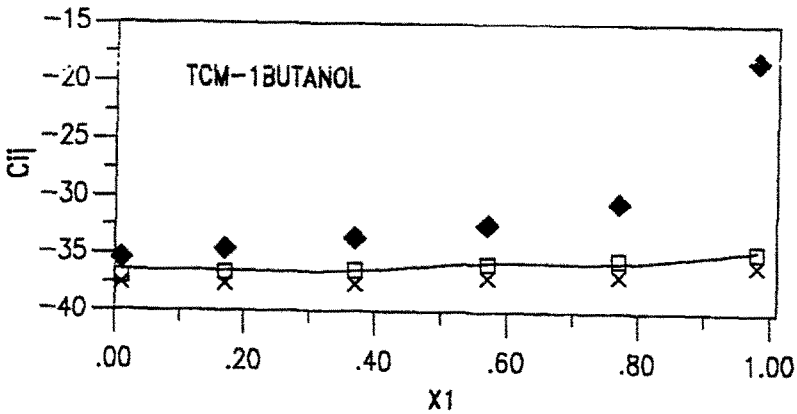


Figure 4: The variation of  $\rho C_{ij}$  with composition for tetrachloromethane (1) + 1-Butanol (2) at 298K.  $\rho C_{11}$  (\*);  $\rho C_{12}$  (□) and  $\rho C_{22}$  (♦). The solid curve represents the  $\rho C_{12}$  predicted by the present theory.

## 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  $\alpha_{21}$  and  $\alpha_{12}$  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 derivatives can be used to get a good approximation for  $G_{ij}$ 's at high pressure by writing.

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

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  $\alpha_{21}$  and  $\alpha_{12}$ . This procedure was followed in finding the coefficients reported in Table 2. The table shows that  $\alpha_{ij}$  can

TABLE: 2

Effect of Pressure on Closure Coefficients

System	Pressure (bar)	Eq. 12		Eq. 17	
		$\alpha_{21}$	$\alpha_{12}$	$\alpha_{21}$	$\alpha_{12}$
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 <sup>a</sup> - 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

<sup>a</sup> 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 arithmetic mean shows mostly a monotonic variation with pressure.

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