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Thermodynamic Properties of Fluids from Fluctuation Solution Theory

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ABSTRACT

Fluctuation Theory develops exact relations between integrals of molecular correlation functions and concentration derivatives of pressure and chemical potential. These quantities can be usefully correlated, particularly for mechanical and thermal properties of pure and mixed dense fluids and for activities of strongly nonideal liquid solutions. The expressions yield unique formulae for the desirable thermodynamic properties of activity and density.

The molecular theory origins of the fluctuation properties, their behavior for systems of technical interest and some of their successful correlations will be described. Suggestions for fruitful directions will be suggested.

INTRODUCTION

Fluctuation Solution Theory is important not only for understanding the molecular processes of mixtures, it also provides general statistical mechanical relationships for certain thermodynamic properties that can be utilized for physical property correlations of mixtures with arbitrary numbers of components. In particular, isothermal concentration derivatives of the chemical potential and pressure are given in terms of molecular correlation functions without any assumption about the form of the intermolecular potential energy and solution properties can be compactly described in terms of matrix notation.

This paper describes certain aspects of interest in fluids at extreme conditions. More complete discussion of the theory and other results can be found in O'Connell(1990) as well as in other articles in the monograph edited by Matteoli and Mansoori(1990).

BASIC EXPRESSIONS FOR MOLECULAR COMPONENTS

Most of the basic expressions from molecular theory will be given here in their general multicomponent form. However, at the end of this section, expressions for many of the special cases described in detail later will also be written.

*Total Correlation Functions*

The earliest work on fluctuation theory was by Kirkwood and Buff (1951) who related integrals of the statistical mechanical total correlation function to the macroscopic manifestations of molecular concentration fluctuations in the grand canonical ensemble. They gave fundamental expressions that connected the matrix of integrals of the total correlation function (TCFI),  $\mathbf{H}$ , to the statistical fluctuations of the elements of the vector of numbers of molecules of each component,  $\mathbf{N}$ , and to the variation of the number of molecules of component  $i$ ,  $N_i$ , with a change of the chemical potential of component  $j$ ,  $\mu_j$ , at fixed temperature,  $T$ , total volume,  $V^T$ , and other chemical potentials,  $\mu_{k \neq j}$ , where  $i$  and  $j$  are an arbitrary pair.

$$[\mathbf{A}]_{ij} \equiv \frac{RT}{N} \left( \frac{\partial N_i}{\partial \mu_j} \right)_{T, V^T, \mu_{k \neq j}} \quad (1a)$$

$$= \left( [(\mathbf{N}\mathbf{N})^T]_{ij} - N_i N_j \right) / N^2 \quad (1b)$$

$$= (\delta_{ij} N_i + N_i N_j [\mathbf{H}]_{ij} / N) / N \quad (2)$$

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Here the total correlation function is defined as the difference between the pair correlation function (or radial distribution function) at a particular distance from a particle center of mass and the average solution value of unity

$$h_{ij} \equiv g_{ij} - 1 \quad (3)$$

the TCFI is the dimensionless spatial integral

$$[\mathbf{H}]_{ij} \equiv H_{ij} \equiv \rho \int h_{ij} d\vec{r} \quad (5)$$

where  $\rho$  is the molar density,  $N/V^T$ , and  $\delta_{ij}$  is the Kronecker delta. All matrices given above are symmetric.

A more desirable quantity is the change of chemical potential of any component  $i$  with the number of molecules of any other component  $j$  at fixed  $T$ ,  $V^T$ , and other mole numbers,  $N_{k \neq j}$ . (the canonical ensemble variables) which is related to elements of the inverse matrix of  $\mathbf{A}$

$$\frac{N}{RT} \left( \frac{\partial \mu_i}{\partial N_j} \right)_{T, V^T, N_{k \neq i}} = [\mathbf{A}^{-1}]_{ij} \quad (5)$$

All of these equations are expressed in terms of the total number of molecules which can be converted to moles with Avogadro's number,  $N_A$ . Expressions in terms of intensive variables involve dividing  $\mathbf{N}$  by  $V^T$  to get concentrations,  $\rho_i \equiv N_i/V^T$ . The result for equation (6) is

$$\frac{\rho}{RT} \left( \frac{\partial \mu_i}{\partial \rho_j} \right)_{T, \rho_{k \neq j}} = [\mathbf{A}^{-1}]_{ij} \quad (6)$$

A set of independent variables in terms of  $V^T$  or  $\rho$  is not the most convenient for many purposes, so a transformation must be done to obtain the Lewis-Randall set  $T$ ,  $F$ ,  $\mathbf{N}$  or  $\mathbf{x}$ . This is achieved in two steps which not only yield chemical potential derivatives with these variables, but also generate a new relation which connects system density and pressure. Thus, the formalism provides equations for both chemical potential (or activity coefficient) and density from Lewis-Randall variables. The final results for binary systems and for the case of one solvent ( $0 < x_1 \leq 1$ ) and multiple solutes ( $x_i < 1$ ) were given by Kirkwood and Buff (1951) who transformed the  $\mathbf{A}$  matrix for this case.

O'Connell (1971) gave matrix expressions for the general case with all solution compositions and introduced full matrix notation. The derivation and the final equations for TCFI will not be repeated here; the details can be found in O'Connell(1990).

The equations are for *derivatives* of the chemical potential, total volume and osmotic pressure. Further steps are needed to obtain the desired properties. In particular, integration of sets of these partial derivatives from a suitable reference state to the solution state is done (O'Connell, 1981), as described below. This feature is both the strength and the challenge of fluctuation solution thermodynamics; it yields activity coefficients as well as densities of mixtures of arbitrary numbers of components in terms of molecular quantities amenable to modeling, but it is formulated in terms of complex expressions and requires reference state information.

### Direct Correlation Functions

In addition to the above formulation in terms of the TCFI, the Ornstein-Zernike Equation (1914) has been used to express the same thermodynamic quantities in terms of

integrals of the direct correlation function. The results are expressed much more simply than in terms of the TCFI and there are no divergences at fluid critical points. The integrated form of the multicomponent O-Z Equation is

$$[\mathbf{H}]_{ij} = [\mathbf{C}]_{ij} + [\mathbf{HXC}]_{ij} \quad (7)$$

where  $[\mathbf{C}]_{ij}$ , the direct correlation function integral (DCFI) is the dimensionless spatial integral of the direct correlation function (dcf)

$$[\mathbf{C}]_{ij} \equiv C_{ij} \equiv \rho \int c_{ij} d\vec{r} \quad (8)$$

The matrix  $\mathbf{X}$  is diagonal with mole fractions

$$[\mathbf{X}]_{ij} \equiv \delta_{ij} x_i \quad (9)$$

The expressions that arise for the quantities of equations (5) and (6) are much simpler in terms of the DCFI. The basic expression relating  $\mathbf{A}$ ,  $\mathbf{H}$ , and  $\mathbf{C}$  arises from combination of Equations (2), (5) and (7).

$$[\mathbf{A}]^{-1} = [\mathbf{X} + \mathbf{XHX}]^{-1} = \mathbf{X}^{-1} - \mathbf{C} \quad (10)$$

This then leads to

$$\frac{\rho}{RT} \left( \frac{\partial \mu_i}{\partial \rho_j} \right)_{T, \rho_{k \neq j}} = \frac{\delta_{ij}}{x_i} - C_{ij} \quad (11)$$

or, in terms of the mole fraction activity coefficient

$$\ln \gamma_i \equiv (\mu_i - \mu_i^o) / RT - \ln x_i \quad (12)$$

the expression is

$$\rho \left( \frac{\partial \ln \gamma_i}{\partial \rho_j} \right)_{T, \rho_{k \neq j}} = 1 - C_{ij} \quad (13)$$

The connection between the canonical and the Lewis-Randall variables for activity coefficients is

$$N \left( \frac{\partial \ln \gamma_i}{\partial N_j} \right)_{T, V, T, N_{k \neq j}} = N \left( \frac{\partial \ln \gamma_i}{\partial N_j} \right)_{T, P, N_{k \neq j}} + \frac{\rho \bar{V}_i \bar{V}_j}{\kappa_T RT} \quad (14)$$

which leads to the activity coefficient derivative

$$\begin{aligned} \frac{N}{\rho \kappa_T RT} \left( \frac{\partial \ln \gamma_i}{\partial N_j} \right)_{T, P, N_{k \neq j}} &= \\ &= \sum_k \sum_l x_k x_l [(1 - C_{ij})(1 - C_{kl}) - (1 - C_{ik})(1 - C_{jl})] \end{aligned} \quad (15)$$

the partial molar volume

$$\frac{\bar{V}_i}{\kappa_T RT} \equiv \left( \frac{\partial P / RT}{\partial \rho_i} \right)_{T, \rho_{j \neq i}} \quad (16a)$$

$$= \sum_j x_j (1 - C_{ij}) \quad (16b)$$

and the reduced bulk modulus

$$\frac{1}{\rho \kappa_T RT} \equiv \left( \frac{\partial P / RT}{\partial \rho} \right)_{T, \mathbf{x}} \quad (17a)$$

$$= \sum_i \sum_j x_i x_j (1 - C_{ij}) \quad (17b)$$

For a component  $i \neq 1$  in a single solvent 1, the osmotic pressure,  $\Pi$ , is related to composition by

$$\frac{N_1}{\rho RT} \left( \frac{\partial \Pi}{\partial N_i} \right)_{T, \mu_1, N_1, N_{j \neq i}} = x_1 \left[ C_{1i} + \sum_j x_j (1 - C_{ij}) \right] \quad i \neq 1 \quad (18)$$

or

$$\sum_{j>1} x_j \left( N \frac{\partial \ln \gamma_j}{\partial N_i} \right)_{T, \mu_1, N_1, N_{k \neq i}} = \sum_{j>1} x_j [(1 - C_{ij}) - (1 - C_{1i})] \quad (19)$$

The general expressions for multicomponent solvents are more complex.

The most desirable properties are the *integrals* of these equations. To actually accomplish this requires that the model for the DCFI be given in terms of the independent variables  $T$  and  $\rho$ , as in traditional equations of state in the van der Waals form. Here, given a model for the  $C_{ij}$  as a function of  $(T, \rho)$ , integration of the set of equations (16) for all  $i$  uses the desired independent variables  $(T, P, x)$  to obtain  $\rho$  from the reference state properties  $T, P_o, \rho_o, x_o$ .

$$\frac{(P - P_o)}{RT} = \sum_i \sum_j \int_{x_{oj}, \rho_o}^{x_j, \rho} \rho_j \frac{(1 - C_{ij})}{\rho} \Big|_{T, \rho_k \neq j} d\rho_j \quad (20)$$

Then, the activity coefficient is obtained by integrating the set of equations (13)

$$\ln \gamma_i = \sum_j \int_{x_{oj}, \rho_o}^{x_j, \rho} \frac{(1 - C_{ij})}{\rho} \Big|_{T, \rho_k \neq j} d\rho_j \quad (21)$$

Although the forms of equations (20) and (21) may imply some complexity in the integrations, Mathias and O'Connell (1981) show how this can be easily accomplished.

For the case of pure components only the limiting case of equations (17) is of interest.

$$\frac{1}{\rho \kappa_T RT} \equiv \left( \frac{\partial P / RT}{\partial \rho} \right)_T = (1 - C) \quad (22)$$

The integrated form of (20) is then

$$\frac{(P - P_o)}{RT} = \int_{\rho_o}^{\rho} (1 - C) \Big|_T d\rho \quad (23)$$

If an equation relating  $(1 - C)$  to  $T$  and  $\rho$  is known, (23) can be integrated directly and either  $P$  or  $\rho$  can be found by knowing  $P_o, \rho_o$  and  $\rho$  or  $P$ . Thus, as shown below, an equation describing compressions of fluids is available.

For the partial molar volume of component (1) at infinite dilution in solvent (2)

$$\frac{\bar{V}_i^\infty}{\kappa_{T2} RT} = (1 - C_{12}^\infty) \quad (24)$$

Finally, for a binary solution one form of the activity coefficient derivatives is

$$\rho \left( \frac{\partial \ln \gamma_1}{\partial \rho_1} \right)_{T, \rho_2} = 1 - C_{11} \quad (25a)$$

$$\rho \left( \frac{\partial \ln \gamma_1}{\partial \rho_2} \right)_{T, \rho_1} = 1 - C_{12} \quad (25b)$$

The expressions for component (2) can be found by exchanging subscripts (1) and (2) in equations (25). For constant pressure derivatives, the relations are

$$\frac{1}{\rho\kappa_T RT} \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = x_2 [(1 - C_{11})(1 - C_{22}) - (1 - C_{12})^2] \quad (26)$$

where

$$\frac{1}{\rho\kappa_T RT} = x_1^2(1 - C_{11}) + 2x_1x_2(1 - C_{12}) + x_2^2(1 - C_{22}) \quad (27)$$

It should be noted that only for pure components (where there is only one DCFI) and for strongly nonideal solutions (where the unlike  $1 - C_{ij}$  are significantly different from the arithmetic or geometric mean of the like  $1 - C_{ii}$  and  $1 - C_{jj}$ ) will correlations have any chance of success. There is a "small difference of large numbers" problem in equation (26) which cannot be avoided by using equations (25) because it reappears in equations (20) and (21). This means that only for the cases of supercritical and solid substances sparingly soluble in liquids, salts and perhaps for partially miscible components can estimated values of the various DCFI be used for accurate predictions. As a result, most practical work has focussed on the pressure effects on pure and mixed liquids and on supercritical and ionic systems.

From a molecular point of view, if a DCFI is less than zero, the (repulsive) excluded volume forces dominate, while if it is greater than zero, attractive and/or long range forces dominate. The former is true for normal pure liquids where the range of  $C$  is from -10 to -1000. There are three cases where the latter occurs. The first is in pure fluids near the critical point where  $C \approx 1$ . The second is in dilute gases at lower reduced temperatures since  $C = -2B\rho + \dots$  with  $B (\leq 0)$  the second virial coefficient. The third case is for pairs of salt components at low concentrations where the Debye-Huckel Limiting Law gives  $C_{ij}^{DHLL} = S_\gamma \rho / 4I^{3/2} + \dots > 0$  where  $S_\gamma$  is related to the solvent dielectric constant and density and  $I$  is the ionic strength (see below).

Equation (7) assumes that the last term (associated with indirect correlations) can be integrated in such a way that the TCFI and DCFI can be separated. The discussion in Chapter 5 of Gray and Gubbins (1984) indicates that for molecular fluids, this either requires that a strong angular condition be obeyed or that the integrals may not be directly connected to microscopic angle-averaged or perturbation correlation functions. In the present work, the DCFI is treated as a macroscopic quantity in the same way that the partition function is in cell or lattice theory models (Reed and Gubbins, 1973). For nearly spherical systems, this lack of connection is not of concern and, in fact, the correlational success obtained for wide varieties of molecular fluids when equations (22) and (23) are used may imply that natural systems follow this formulation. On the other hand, use of microscopic models directly in the integral of equations (9) may not be appropriate for some polar and nonspherical molecular components.

## BASIC EXPRESSIONS FOR SPECIES FROM REACTIVE COMPONENTS

The above relations are rigorously true for atomic and molecular components, but there are other situations of interest in fluids. One for which the fluctuation thermodynamics has been explored in some detail involves cases where the components used to make up the thermodynamic system can react (dissociate, associate, solvate) to form new species. Examples of such reactive components include electrolytes that ionize, organic acids that

dimerize and absorbing solvents for acid gases which solvate. While the molecular, or *component* treatment is still correct, a more desirable goal is to model TCFJ and/or DCFI between the *species* which are actually, or conceptually, present.

This lead to correlations with parameters from, for example, ions, rather than salts. Then, multicomponent expressions can require minimal or no information beyond single- or binary-component systems. Thus, for example, completely reacting systems, e.g., strong electrolytes, would have no "salt" parameters nor equilibrium constants. (For partially reacting systems, both would be needed.) Whether the result would be the same as for other "chemical theories" where the situation often involves too many parameters to fit to the system data, or if the species quantities can be obtained from other systems is still to be investigated.

The fact that the species arise from components via well-defined reactions leads to a certain "connectedness" that appears in the correlation function integrals. This is separate from the long-ranged behavior of electrostatic forces and of site-site developments. Perry et al. (Perry and O'Connell, 1984; Perry, et al., 1988) developed the general expressions for fluctuation thermodynamic properties in multicomponent systems. Their complexity precludes repeating all of them here. However, the case of completely reacting components is given so that the results can be implemented for strong electrolyte models (see below).

The essential equations are again of the vector and matrix form. For a set of  $n_0$  components whose numbers of moles are given by a vector  $\mathbf{N}_0$  with  $n_0$  elements, the reactions will yield a set of  $n$  species whose numbers of moles are given by a vector  $\mathbf{N}$  with  $n$  elements. The reactions (specifically the stoichiometric coefficients) lead to a  $n \times n_0$  projection matrix identified as  $\mathbf{W}$ . Thus

$$\mathbf{N} = \mathbf{W}\mathbf{N}_0 \quad (28)$$

While Perry and O'Connell (1984) give general expressions, the most interesting result for the present purposes with electrolyte solutions is that for complete dissociation (Perry, et al., 1988). For two components  $i$  and  $j$  which dissociate into  $\nu_{i\alpha}$  and  $\nu_{j\beta}$  species, the desired component  $j$  concentration derivative of the component  $i$  activity coefficient is not only given by the molecular DCFI of equation (1.19) above,  $C_{0ij}$ , it can also be expressed in terms of DCFIs between  $\alpha\beta$  pairs of the species from the reactions. With this notation (subscript  $_0$  for components), the result is

$$\rho \left( \frac{\partial \ln \gamma_i}{\partial \rho_{0j}} \right)_{T, \rho_{0k \neq j}} = 1 - C_{0ij} \quad (29)$$

where

$$\rho \equiv N/V^T \quad (30)$$

$$N \equiv \sum_i \sum_{\alpha} \nu_{i\alpha} N_{0i} \quad (31)$$

$$\rho_0 \equiv N_0/V^T \quad (32)$$

$$N_0 \equiv \sum_i N_{0i} \quad (33)$$

$$\nu_i \equiv \sum_{\alpha} \nu_{i\alpha} \quad (34)$$

$$C_{0ij} = \sum_{\alpha} \sum_{\beta} \nu_{i\alpha} \nu_{j\beta} C_{\alpha\beta} / \nu_{\alpha} \nu_{\beta} \quad (35)$$

In essence, the development shows that for complete reactions, a direct substitution of the proper collection [equation (35)] of species DCFI can be made for the component DCFI to obtain the fluctuation thermodynamic properties of such solutions. As shown below, this leads to a particularly simple development for strong electrolytes. Unfortunately, the general case of partial reactions is much more complicated since the general formulation involves derivatives of the equilibrium extent of reaction which must be connected to the equilibrium constant. This case has not been addressed in any detail.

## CORRELATIONS AND RESULTS FOR VARIOUS CASES

### *Pure Liquids*

The first work to establish a useful correlation of fluctuation thermodynamic properties was that of Brelvi and O'Connell (1972) who described a one-parameter form of corresponding states for the DCFI with a characteristic volume to scale the density of a wide variety of pure fluids. This led to a simple and reliable correlation for the change of density of liquids when pressurized. Given the saturated molar volume at ambient conditions, the density at a higher pressure could be predicted to within 1% if the temperature were less than the critical. This work was taken a step further by Huang and O'Connell (1987) with an extremely accurate and reliable 3-parameter corresponding states correlation over the same liquid range. In this case the characteristic parameters were in volume,  $V^*$ , temperature,  $T^*$ , and DCFI,  $C^*$ .

Figure 1 shows the behavior of the scaled pressure over wide ranges of density along various reduced isotherms. There turns out to be very little temperature variation of the DCFI as implied by the similarity of the curves at similar densities. In fact, there is even a density where no variation of  $1 - C$  with  $T$  is found - at lower densities the DCFI becomes less negative with temperature while at high densities the opposite occurs. The strong, and universal, density dependence of the DCFI leads to the correlation using  $C^*$  and  $V^*$  at the temperature independent point as well as  $T^*$  at about  $0.95T_c$ . Table 1 shows some results for reduced pressure,  $PV^*/RT$ , and temperature,  $T/T^*$ , for the nearly 300 substances and mixtures using the Huang (1986) correlation. The predicted densities all the way to very high pressures are generally within 1%. For truly predictive purposes, only the characteristic volume cannot be estimated to the required accuracy (because of great sensitivity to it) from group contributions. The mixture results for both the Brelvi and Huang methods are commensurate with their accuracies for pure components. With estimates of liquid heat capacities, these correlations can also be used to obtain speeds of sound in nonelectrolytes, liquid metals and polymers.

Temperature-independent DCFI indicate a balance between attractive and repulsive forces. The question of whether the correlation form arises naturally out of current theories and equations of state was investigated by Mathias (1978), Campanella (1984), Telotie (1985) and Huang (1986, 1987). The conclusion is that the density variation of real liquids is weaker at lower densities than for rigid bodies. (At the critical point, a real fluid has a DCFI value of 1 whereas rigid bodies always have the  $DCFI \leq 0$ . This difference dominates much of the liquid range.) The variations are about the same at very high densities if the rigid body spherical or nonspherical equations include the temperature and density dependent hard sphere diameter of the Weeks-Chandler-Andersen(WCA) reference fluid (see, e.g., Reed and Gubbins, 1973). However, at normal liquid densities, no linear density term, (such as in a generalized van der Waals equation), is adequate to correct the rigid-body equation to experimental results for real fluids. This suggests that perturbation theories based on rigid bodies must have elaborate corrections to achieve good descriptions of TCFI and DCFI. Finally, even those cubic equations of state which

give reliable saturation densities give poor compressibilities; their form does not agree with the correlation. This indicates that their accuracy with vapor-liquid equilibria, whether with good or poor saturation densities, is not a result of their isotherms being correct. They apparently have compensating errors.

### *Partial Molar Volumes at Infinite Dilution*

The second quantity to be correlated by DCFI models was the partial molar volume at infinite dilution for gases in liquids (Brelvi and O'Connell, 1972) and for salts in water (Cooney and O'Connell, 1987) over wide ranges of conditions and substances. The DCFI of equation (24) at infinite dilution is expressed in terms of reduced solvent density. Brelvi and O'Connell's correlation (1972) also involved only the characteristic volumes of the gas and the solvent, but was reasonably accurate for many types of substances over wide ranges of solvent density (and temperature). Table 2 shows some of the comparisons with data.

Cooney and O'Connell's examination (1987) of aqueous solution salt-water (unlike) DCFI found that  $C_{ij}^\infty$  could be described by a 2-parameter correlation in terms of water density and temperature to cover the range from water at its critical point all the way to room temperature and 100MPa. One of the parameters seemed to depend only on the charge type of the salt. Table 3 shows some of the comparisons with data for various salts. Preliminary work indicates that the general behavior of this correlation is preserved by NaCl at supercritical temperatures as well.

The forms of the above correlations also have implications for solute  $i$  partial molar volumes at the solvent  $j$  critical point (where  $\kappa_j$  goes to  $\infty$  so  $1 - C_{jj}$  goes to zero). Brelvi's correlation indicates that at the solvent critical point  $C_{ij}$  for supercritical  $i$  remains positive and finite. This is consistent with the observation that at the solvent critical point, the gas partial molar volume approaches  $+\infty$ . At the same time, Cooney's work shows that  $C_{ij}$  is positive and independent of temperature below about 2.8 times the water critical density, becoming nearly independent of density at about twice the critical. Thus, the salt partial molar volume goes to  $-\infty$  at the water critical. These observations can be summarized as

$$\begin{aligned} \frac{\bar{V}_i^\infty}{\kappa_T RT} &\equiv \lim_{x_j \rightarrow 1} \frac{\bar{V}_i}{\kappa_T RT} \\ &= \lim_{x_j \rightarrow 1} (1 - C_{ij}) \\ &\equiv (1 - C_{ij}^\infty) \end{aligned} \quad (36)$$

$$\rho_j^{Pure} \bar{V}_i^\infty = \frac{1 - C_{ij}^\infty}{1 - C_{jj}^{Pure}} \quad (37)$$

and

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$$\lim_{j \rightarrow \text{critical}} \left\{ \begin{array}{l} \kappa_j = \lim_{j \rightarrow \text{critical}} \frac{1}{\rho_j^c RT (1 - C_{jj}^{\text{Pure}})} \\ (1 - C_{jj}^{\text{Pure}}) = 0 \\ \rho_j^{\text{Pure}} \bar{V}_i^\infty = +\infty \text{ for } T_i^c < T_j^c \\ \rho_j^{\text{Pure}} \bar{V}_i^\infty = -\infty \text{ for } T_i^c > T_j^c \end{array} \right. \quad (38a)$$

$$(38b)$$

There are some exceptions to (38), especially if the critical temperatures of the components are close. Of course, the variation of  $\kappa$  near the critical follows nonclassical, or critical-scaling, behavior (see, e.g., Rowlinson and Swinton, 1983), implying that  $1 - C_{jj}^{\text{Pure}}$  is strongly nonclassical near its zero value. The variation of  $1 - C_{ij}^\infty$  shows weak nonclassical behavior allowing correlations such as that of Cooney to be accurate quite close to the solvent critical.

### Nonelectrolyte Liquid Solutions

As mentioned above, there is not much likelihood of using estimated values of DCFI to obtain activity coefficients in miscible nonelectrolyte solutions because of the form of equation (1.21). However, this sensitivity can be exploited to test models for activities by taking their derivatives to arrive at solution DCFI and comparing them with data. This has been done a few times as indicated Hamad, et al. (1989) and also by Brelvi (1972) and Wooley (1987, 1990).

Further, Brelvi and O'Connell (1972), Mathias and O'Connell (1981) and Campanella, et al. (1987) demonstrate application of simple models for the DCFI which describe liquids with dissolved supercritical components.

The objective of the correlation is to obtain expressions for fugacities of liquid components which could be used for vapor-liquid equilibria calculations. For supercritical components, the composition range is mostly dilute, so the Henry's Law reference state was used. In addition, the pressure is usually elevated so that the isothermal fugacity depends on both composition and pressure. As illustrated by Prausnitz, et al. (1986), a traditional way of writing this expression is

$$\ln \hat{f}_i(T, P, \mathbf{x}) = \ln [x_i H_i(T)] + \ln \gamma_i^*(T, \mathbf{x}) + \int_{P_i^0}^P \frac{\bar{V}_i(T, p, \mathbf{x})}{RT} \Big|_{T, \mathbf{x}} dp \quad (39)$$

where the dependence of the quantities on solution state,  $T, P, \mathbf{x}$ , are shown here explicitly. These include Henry's Constant,  $H_i$ , at the reference pressure,  $P_i^0$ , the partial molar volume at the solution state,  $\bar{V}_i$  and the unsymmetric convention activity coefficient,  $\gamma_i^*$ , with

$$\lim_{x_i \rightarrow 0} \ln \gamma_i^* = 0 \quad (40)$$

At the low concentrations usually encountered, it is common to use the Krichevsky - Ilinskaya (KI) approximations

$$\ln \gamma_i^{*KI}(T, \mathbf{x}) \simeq -A_{ii}(T) [2x_i - x_i^2] \quad (41)$$

$$P_i^0 \equiv P_j^{\text{Sat}} \quad (42)$$

$$\int_{P_i^o}^P \frac{\bar{V}_i(T, P, \mathbf{x})}{RT} \Big|_{T, \mathbf{x}} dp \simeq \bar{V}_{ij}^{\infty}(T) \left[ \frac{(P - P_j^{Sat})}{RT} \right] \quad (43)$$

As discussed by Mathias and O'Connell(1981), the composition effect [equation (41)] and the pressure effect [equation (43)] are of opposite sign and can even cancel. The apparent linearity of a plot of  $\ln(y_i \hat{\phi}_i P / x_i)$  [with  $\hat{\phi}_i(T, P, \mathbf{y})$  the vapor phase fugacity coefficient] versus either  $P$  or  $x_i$  is a result of complex cancellation (See, e.g., Orentlicher and Prausnitz, 1964).

Campanella, et al (1987), building on the work of Mathias and O'Connell (1981), described the volumes and activities for a large variety of liquids with supercritical components while avoiding estimating the two terms of opposite sign. Their fundamental equation for the fugacity is

$$\ln \hat{f}_i(T, P, \mathbf{x}) = \ln [x_i H_{iR}(T)] + \ln \gamma_i^+(T, P, \mathbf{x}) \quad (44)$$

where the reference state for the activity coefficient is carefully defined

$$\lim_{\substack{x_R \rightarrow 1 \\ P \rightarrow P_R^{Sat}}} \gamma_i^+(T, P, \mathbf{x}) = 1 \quad (45)$$

with component  $R$  being a reference component which is a liquid at the system temperature. All solutions use this state for their reference composition and pressure. The model was based on a two-parameter corresponding states form of  $C_{ij}$  from van der Waals equation and involved a single binary parameter for each solvent/solute pair of components. The key to the correlation's success arises uniquely from fluctuation solution theory by integrating Equation (20) to find the solution density and Equation (21) to find the activity coefficient  $\gamma_i^+$  from a pure solvent reference state. This worked extremely well for many different systems as indicated in Table 4. One appealing aspect of the work was that the densities and deviations from Henry's Law in a single solvent  $j$  were quite insensitive to the value of the model's only binary parameter. However, the accuracy did depend strongly on the infinite dilution fugacities, i.e., Henry's Constant,  $H_{ij}$ .

An accurate and convenient way to obtain  $H_{ij}$  is with a particular limit for the integration of Equation (20) for supercritical component  $i$ . Taking the limits to be infinite dilution in solvent  $j$  and infinite dilution in solvent  $R$  connects the two Henry's Constants  $H_{ij}$  and  $H_{iR}$  via the limiting activity coefficient.

$$\gamma_i^{+\infty} \equiv \lim_{x_j \rightarrow 1} \gamma_i^+ \quad (46)$$

$$= \frac{H_{ij}}{H_{iR}} \quad (47)$$

$$= \int_{\rho_R^{Pure}}^{\rho_j^{Pure}} \frac{1 - C_{ij}}{\rho} \Big|_{T, \rho_k \neq j} d\rho_j \quad (48)$$

Then, the activity of a supercritical component at low concentrations in a solvent can be predicted from Henry's Constant in the Reference solvent, the densities of both pure solvents and a good model for the  $C_{ij}$ . The definition of "good" is to have an accurate enough value of the binary constant to obtain Henry's Constant,  $H_{ij}$ , in the desired solvent  $j$  from equation (47). It was found that a temperature independent quantity was often adequate for temperature variations of more than 100 K.

This same technique has been used successfully for Henry's constants in mixed solvents,  $H_{im}$ . In this case, the results can be sensitive to values of the mixed solvent density, particularly in aqueous solutions. Table 5 gives some of the mixed solvent results of Campanella, et al. (1987). The accuracy is uniquely high for aqueous systems and uses only binary information to predict ternary and higher order systems.

At the present time, models for vapor-liquid equilibria are best written in terms of full equations of state. This technique avoids the inevitable discontinuities of fugacities in the critical region when the liquid phase value uses activity coefficients and the vapor phase uses fugacity coefficients obtained from different models. Their limitation is the difficulty of finding mixing rules for their parameters that allow predictions, particularly in the liquid phase. The correlation of Campanella, et al. (1987) is primarily intended to guide mixing rule formulation and provide insight into liquid behavior, though the work showed that the model can also be useful with the gas phase virial or other equations of state for systems well removed from their critical lines.

### *Strong Electrolyte Solutions*

A final area of application of Fluctuation Solution Theory is strong electrolytes. As mentioned above, the formalism for species of reactive components encompasses all systems including partially reacting substances, but these have not been addressed because the basic modeling for charged species has not been completed.

Ionic species involve an additional complexity associated with their long-range electrostatic forces. While the dcfs diverge because they vary as  $r^{-1}$  at long distances, the reactive component treatment shows how charge neutrality requires that all of these effects cancel out for thermodynamic purposes. Thus, there is a convergent dcf

$$c_{ij}^0 \equiv c_{ij} + \frac{z_i z_j e^2}{kTr} \quad (49)$$

which is integrated to obtain a convergent DCFI,  $C_{ij}^0$ . It is this quantity that is used in the formulae given above.

The infinite dilution limits of the various  $C_{ij}^0$  are well determined. The limiting solvent - solvent DCFI,  $1 - C_{11}^{Pure}$ , is the pure solvent bulk modulus,  $\rho/\kappa_{T1}^{Pure} RT$ . The solvent - salt DCFI,  $1 - C_{12}^\infty$ , is  $\bar{V}_{02}^\infty(T)/\nu_2 \kappa_{T1}^{Pure} RT$ . The salt - salt DCFI,  $C_{22}^{0\infty}$ , must obey the Debye-Huckel Limiting Law

$$C_{22}^{0DHLL} = \lim_{x_2 \rightarrow 0} C_{22} = \lim_{x_2 \rightarrow 0} \left[ \sum_i \sum_j \nu_{i2} \nu_{j2} z_i^2 z_j^2 S_{\gamma 1} \rho / \nu_2^2 \right] I^{-1/2} \quad (50)$$

where the sums are over all ions in salt 2 [they arise from Equation (35)], the ionic charges are  $z_i$ , the molar ionic strength is

$$I \equiv \sum_{ions} \nu_{i2} z_i^2 N_{02} / V^T \quad (3.17)$$

$$\equiv \omega_2 \rho x_{02} \quad (51)$$

with  $x_{02} \equiv N_{02}/N$  and the solvent properties are in

$$S_{\gamma 1} \equiv \left[ \frac{2\pi e^6 N_A}{\epsilon_1^3 (kT)^3} \right]^{1/2} \quad (52)$$

with  $e$  the electronic charge and  $\epsilon_1$  the solvent dielectric constant. Obviously,  $C_{22}$  goes to  $\infty$  at zero salt concentration. It should also be noted that the development also leads naturally to the higher order activity coefficient term for unsymmetric salts given by Friedman (1962).

The theoretical work reviewed by Blum (1980) and Stell, et al. (1981) as well as used by Krienke and Weigl (1988), indicates that the dcf can be split into contributions from long-range (ionic and multipolar electrostatic) and short-range forces. Although Stell et al. explicitly expand the electrostatic effects for ions and dipoles in a series in the inverse Debye length

$$\kappa \equiv 2^{3/2} e \left[ \frac{\pi N_A}{\epsilon_1 k T} \right]^{1/2} \quad (53)$$

the series converges only for the dcf and  $C_{22}^0$  but every term in the series contributes to  $C_{12}$  and  $C_{11}$ . Thus, a thermodynamic approach must be taken to obtain the correct macroscopic result for these DCFI. Use of higher order DCFI symmetry leads to the Debye-Huckel Limiting Law electrostatic terms for  $C_{12}$  and  $C_{11}$ . The results are

$$C_{12}^{DHLL} = -\frac{3}{4} \left. \frac{\partial \ln \epsilon_1}{\partial \ln \rho_1^{pure}} \right|_T \frac{\omega_2 e^2 \kappa}{\epsilon_1 k T} \quad (54)$$

and

$$C_{11}^{DHLL} = -\left( 2 \left. \frac{\partial^2 \ln \epsilon_1}{\partial (\rho_1^{pure})^2} \right|_T - 3 \left[ \left. \frac{\partial \ln \epsilon_1}{\partial \rho_1^{pure}} \right|_T \right]^2 \right) \frac{\kappa^3 \rho}{16\pi} \quad (55)$$

These lead to the expressions used by Redlich and Meyer (1964) and Gucker (1933) for the electrostatic corrections to the salt partial molar volume and solution compressibility, respectively.

While Extended Debye-Huckel (EXTDH) expressions can also be derived, as shown by Perry, et al. (1988), an examination of a more fundamental aspect may be needed. For example, though much research on electrolytes has been done over the years, little attention seems to have been paid to which set of variables is the most effective in modeling efforts -  $(T, P, x_2)$ ,  $(T, \rho_1, \rho_2)$  or  $(T, \mu_1, x_2)$ .

In particular, it has been recently asserted (Friedman, 1972; Pailthorpe, et al, 1984; Archer, 1989) that a more fruitful approach may be to recognize that the Debye-Huckel expressions involve an incompressible McMillan-Mayer (1945) system with the solvent modeled as a continuous dielectric whose chemical potential does not change as solute is added. As a result, it is felt that the effects of finite ion size and molecular behavior of the solvent would appear in the short-range dcfs and DCFIs that involve the solvent, but that solute-only terms would not contain anything but electrostatics. The general McMillan-Mayer fluctuation property is

$$\frac{N}{RT} \left( \frac{\partial \mu_i}{\partial N_j} \right)_{T, VT, \mu_k \neq i} = 1/[A]_{ij} \quad (56)$$

$$= N / (\delta_{ij} N_i + N_i N_j [\mathbf{H}]_{ij} / N) \quad (57)$$

so for a single-salt(2), single-solvent(1) system

$$N \left. \frac{\partial \ln \gamma_2}{\partial N_2} \right|_{T, VT, \mu_1^{pure}} = \frac{1}{x_1 + x_1^2 \mathbf{H}_{22}} \quad (58)$$

$$= (1 - C_{22}) - \frac{(C_{12})^2}{x_1 - C_{11}} \quad (59)$$

These derivatives should be compared to the two given in equation (14). The form suggests that if  $(1 - C_{22})$  does have solvent effects, these might be removed by the extra term more effectively than does the conversion of (14).

One indication of whether this is a useful direction to pursue comes from plotting the various derivatives after the Limiting Law has been subtracted. Figure 2 shows them for NaCl at 298.15K while Figure 3 shows them for LiCl at 298.15K. Similar results have been found for NaBr and LiCl up to saturation. Though the scale of the graphs is large, predicted values must be determined to within  $\pm 2$  units. Thus, while not obvious from the figures, it turns out to be true that the McMillan form is more easily modeled and shows much better ionic additivity than does the Kirkwood-Buff derivative. A hint of this can be detected by the different ordering of the models at higher concentrations. The Lewis-Randall form appears to be easier to describe mathematically but it shows the greatest deviations from ionic additivity. Work is in progress to implement this finding into a practical model for density and activity of aqueous salt solutions.

## CONCLUSIONS

The unique form of Fluctuation Solution Theory has led to a number of useful correlations of fluid thermodynamic properties based on macroscopic parameterizations. Using pure component properties at ambient pressures, results have been obtained for densities of pure and mixed compressed liquids, partial molar volumes and solution densities, and activity coefficients of supercritical substances in liquids. Initial understandings of useful forms for aqueous electrolytes have been made. Much remains to be done in treatments of this type as well as to connect the empirical success described here to molecular theories for the correlation functions.

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## FIGURE CAPTIONS

Figure 1. Corresponding States Behavior of Pressure Effects on Liquid Density.

Figure 2. Convergent Activity Coefficient Derivatives for NaCl at 298.15K.

Figure 3. Convergent Activity Coefficient Derivatives for LiCl at 298.15K.

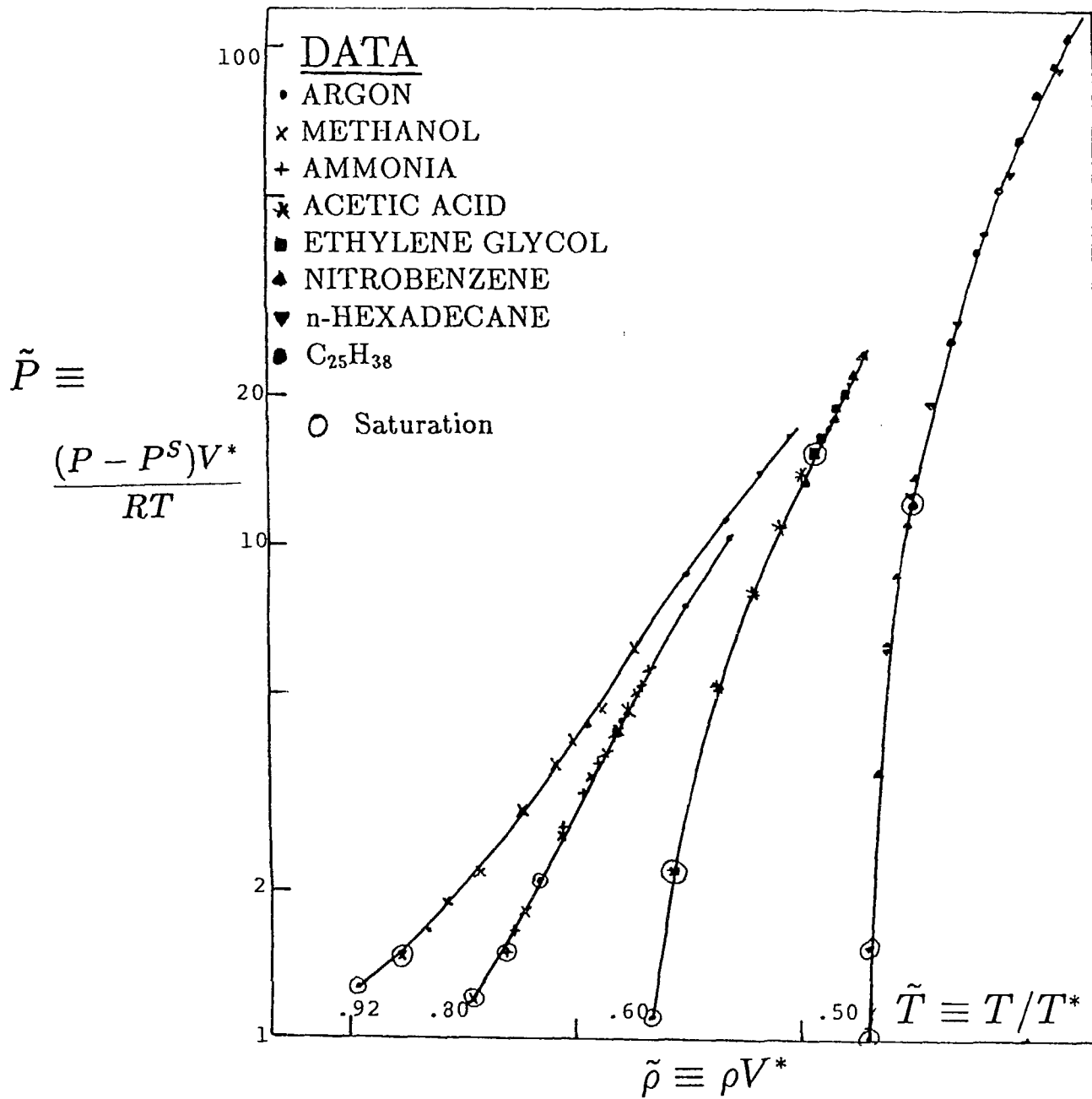


FIGURE 1



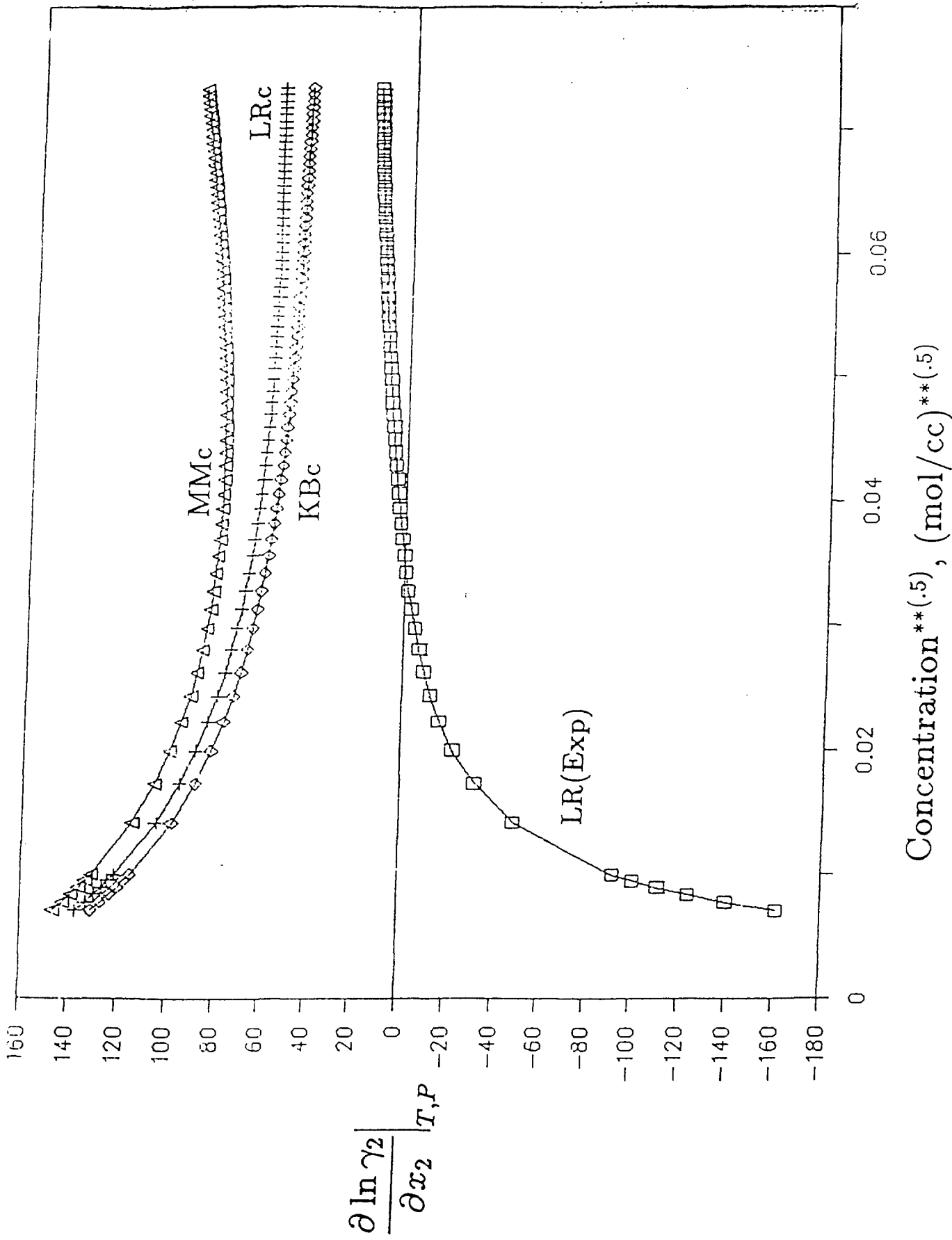


FIGURE 2

FIGURE 3

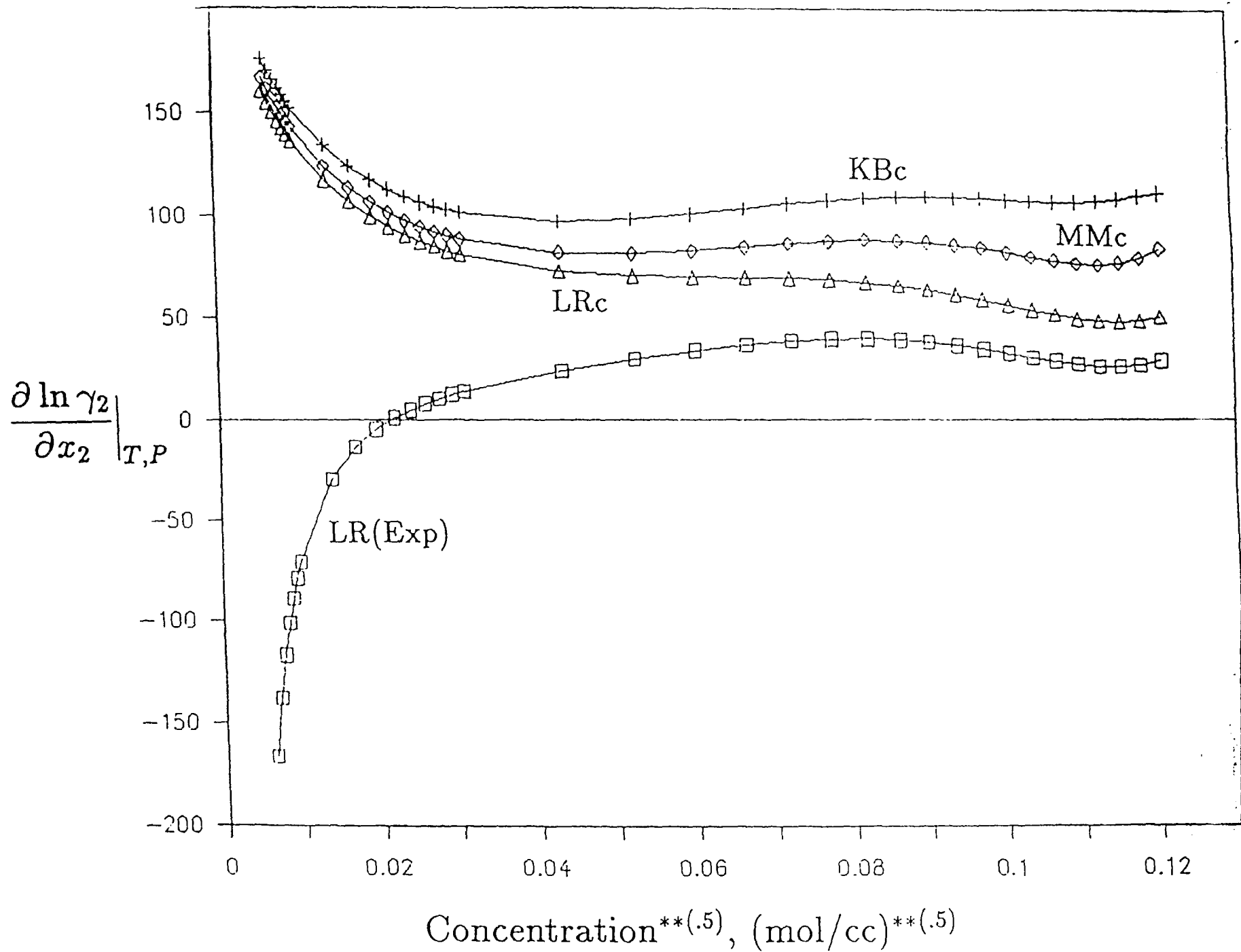


Table 1.  
 CHARACTERISTIC PARAMETERS AND COMPARISONS  
 WITH LIQUID COMPRESSION DATA

From Y-H. Huang (1986).

Substance	$-C^*$	$V^*, \frac{cm^3}{mol}$	$T^*, K$	$PV^*/RT$	$T/T^*$	AAE, %
<i>Ar</i>	16.5	28.82	150	0-4.5	0.7-1.0	0.5
<i>Bi</i>	18.3	27.71	751	0-4.8	.7-1.3	1.1
<i>CH<sub>3</sub>OH</i>	16.5	39.59	492	0-1.6	0.6-1.0	1.1
<i>NH<sub>3</sub></i>	12.2	26.01	381	0-2.2	0.7-0.8	1.8
<i>(CH<sub>2</sub>OH)<sub>2</sub></i>	34.0	59.61	603	0-2.4	0.5-0.6	0.4
<i>CCl<sub>2</sub>F<sub>2</sub></i>	37.3	75.97	373	0-1.1	0.7-0.9	1.5
<i>Acetic Acid</i>	32.8	55.78	494	0-1.1	0.6-0.7	0.3
<i>Squalene</i>	223.5	541.49	594	0-43	0.5-0.6	0.6
<i>Ethylene Carbonate</i>	68.3	65.28	646	0-1.1	0.5-0.6	1.4
<i>Si(-OCH<sub>3</sub>)<sub>4</sub></i>	52.8	122.75	402	0-1.2	0.7-0.9	1.1
<i>KCl</i>	16.9	20.58	1526	0-1.4	0.7-0.9	1.1
<i>(n - C<sub>7</sub>H<sub>15</sub>)<sub>4</sub>NBF<sub>4</sub></i>	239.3	561.31	886	0-33	0.4-0.6	0.4
<i>Silicone Oil</i> <i>(Bayer M1000)</i>	396.9	1.0225 <sup>+</sup>	522	0.9 - 1.1 <sup>+</sup>	0.5-0.6	0.3
<i>Poly(cyclohexyl- methacrylate)</i>	131.0	1.0646 <sup>+</sup>	1173	0.9 - 1.1 <sup>+</sup>	0.34-0.4	0.8

<sup>+</sup>  $cm^3/gm$  and  $\rho V^*$

Table 2.  
 PARTIAL MOLAR VOLUMES AT INFINITE DILUTION OF GASES IN LIQUIDS  
 From S. W. Brelvi (1972).

Solute (1)	Solvent(2)	T, K	$V_2, \frac{\text{cm}^3}{\text{mol}}$	$V_{1,Calc}^\infty, \frac{\text{cm}^3}{\text{mol}}$	$V_{1,Exp}^\infty, \frac{\text{cm}^3}{\text{mol}}$
$CH_4$	$n - C_6H_{14}$	298	132.9	59.9	60.2
$H_2$	$n - C_8H_{18}$	403	184.8	68.4	63.6
			182.3	62.8	58.0
			180.0	57.6	53.3
		473	207.6	104.6	110.3
			201.9	86.2	87.6
			197.7	77.1	72.7
$SO_2$	$C_6H_5Cl$	298	100.9	47.7	47
$O_2$	$CH_3OH$	273	39.6	43.2	42
		298	40.6	48.0	45
		323	41.8	54.7	50
$CH_4$	$H_2O$	273	18.01	37.0	36
		298	18.06	37.4	37
		323	18.22	38.7	38

Table 3.

## PARTIAL MOLAR VOLUMES OF SALTS IN WATER

From W.R. Cooney and J.P. O'Connell (1987)

$$\frac{\bar{V}_S^\infty}{\kappa_w RT} = a(1.0 - 7.0 \times 10^{-9} \exp[4500/T]) \exp(106.1 \rho_w) + b$$

Salt	a	b	$\rho_w V_w^\infty$	T, K	Err in $\bar{V}_S^\infty$ , %
<i>CaCl</i> <sub>2</sub>	0.1458	-34.83	2.7-3.1	323-473	0.6
<i>HCl</i>	0.0857	-14.15	2.7-3.1	298-473	0.3
<i>NH</i> <sub>4</sub> <i>Cl</i>	0.1477	-19.01	2.7-3.1	323-473	0.3
<i>K</i> <sub>2</sub> <i>SO</i> <sub>4</sub>	0.1887	-34.55	2.7-3.1	323-473	0.7
<i>NaCl</i>	0.0790	-12.72	1.9-3.5	273-623	2.0
<i>SrCl</i> <sub>2</sub>	0.1457	-33.91	2.7-3.1	323-473	0.5

Table 4.

VAPOR-LIQUID EQUILIBRIA FOR BINARY SOLUTIONS WITH ONE  
 SUPERCRITICAL COMPONENT

From E.A. Campanella, P.M. Mathias and J.P. O'Connell, (1987).

Gas(1)	Solvent(2)	T, K	$x_1$ Max	$x_1^{Err}$ , RMS	$x_1^{Err}$ Max
$N_2$	$n - C_6H_{14}$	311-444	0.49	0.0089	0.0205
$CO$	$CH_3OH$	294-413	0.08	0.0028	0.0049
$H_2$	$NH_3$	273-373	0.15	0.0003	0.0009
$CH_4$	$m - CH_3C_6H_4OH$	463-663	0.21	0.0087	0.0303
$H_2$	<i>Quinoline</i>	462-702	0.21	0.0010	0.0022
$H_2$	$1 - CH_3C_{10}H_7$	463-702	0.21	0.0032 <sup>+</sup>	0.0073 <sup>+</sup>
$H_2$	$(C_6H_{10})_2$	463-702	0.42	0.0078 <sup>+</sup>	0.0196 <sup>+</sup>
$H_2$	"CLPP" <i>Coal Oil</i>	463-623	0.22	0.0028 <sup>+</sup>	0.0048 <sup>+</sup>

<sup>+</sup> Predicted Using  $H_2$  - Quinoline Henry's Constant

Table 5.  
 SOLUBILITY OF GASES IN MIXED SOLVENTS  
 From E.A. Campanella, P.M. Mathias and J.P. O'Connell, (1987).

Gas(1)	Solvent (2)	Solvent(3)	T, K	No. Data	$H_{1m}^{Err}, \%$
$N_2$	Ethanol	Ethylacetate	298	9	1
$CO$	Benzene	Aniline	298	5	4
$C_2H_6$	Methanol	Acetone	298	8	3
$n - C_4H_{10}$	Acetone	n-Propanol	298	11	3
$Ar$	Ethylene Glycol	Water	283-298	36	3
$O_2$	Ethanol	Water	273-313	37	6
$CO_2$	n-Propanol	Water	283-313	46	7