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THERMODYNAMIC PROPERTIES OF STRONGLY NONIDEAL FLUID MIXTURES FROM AN EXTENDED QUASI-CHEMICAL THEORY

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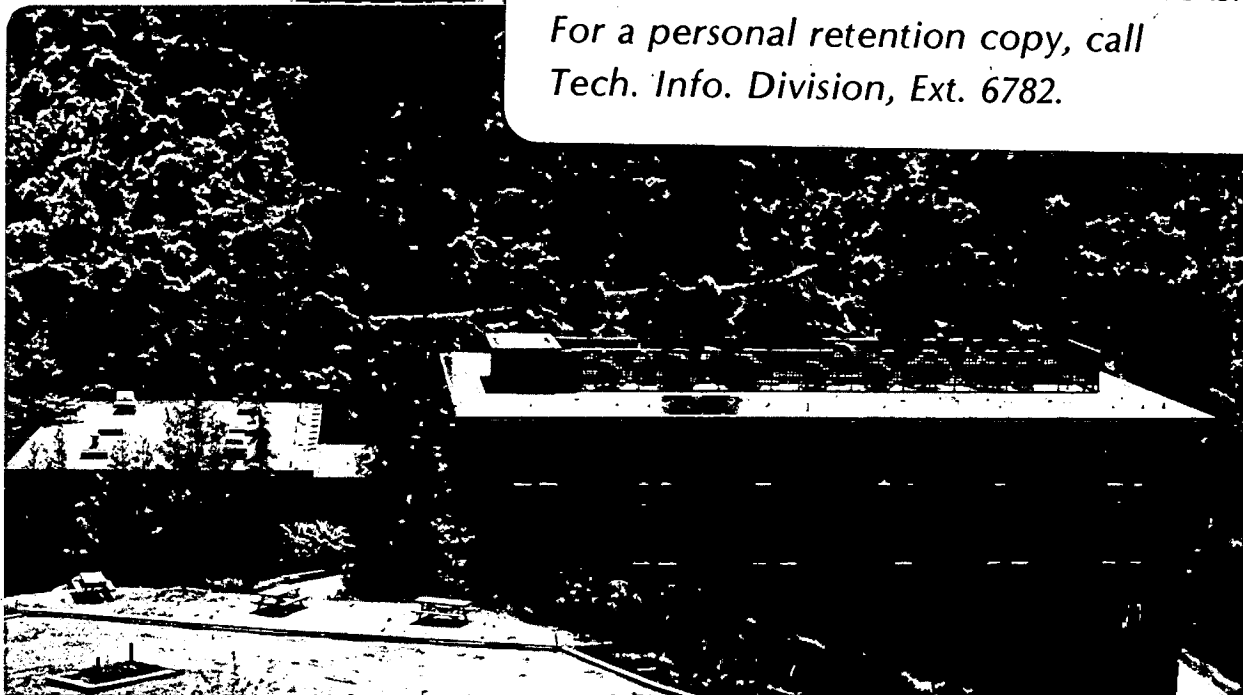
THERMODYNAMIC PROPERTIES OF STRONGLY NONIDEAL FLUID  
MIXTURES FROM AN EXTENDED QUASI-CHEMICAL THEORY

D. Dimitrelis and J.M. Prausnitz

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THERMODYNAMIC PROPERTIES OF STRONGLY NONIDEAL FLUID MIXTURES  
FROM AN EXTENDED QUASI-CHEMICAL THEORY

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ABSTRACT

In his later years, E.A. Guggenheim recognized that the exchange energy in his quasi-chemical theory of mixtures is really a free energy. Proper use of quasi-chemical theory contains an entropic contribution which must also be considered in calculating deviations from random mixing. Methods for including this entropic contribution are discussed here.

When Guggenheim's quasi-chemical theory is coupled with a two-fluid theory of mixtures and a suitable reference system, we obtain an equation of state that may be particularly useful for fluid mixtures showing large deviations from ideality.

## INTRODUCTION

Chemical engineers in process design are increasingly confronted with prediction of phase equilibria for widely asymmetric mixtures, that is, mixtures of molecules which differ significantly in size and shape or intermolecular potential. While many suitable equations of state are available for simple mixtures of nonpolar molecules (such as light hydrocarbons), these equations of state, with standard mixing rules, are not adequate for predicting thermodynamic properties of highly nonideal mixtures.

The most important step in extending an equation of state to mixtures appears to be the proper choice of mixing rules. Density-dependent mixing rules based on the local composition concept, as suggested by Whiting (1981,1982) and also by Mollerup (1981), suggest significant improvement over the usual van der Waals mixing rules.

In this work, Guggenheim's quasi-chemical theory is used as a point of departure for deriving new mixing rules. The quasi-chemical theory has been extended to take into account the effect of both energy and entropy on nonrandom mixing. In relatively simple cases (nonpolar molecules), the entropic effect can be related directly to molecular size. The terms which account for nonrandomness due to energy differences are similar in form to those in Wilson's equation but they have been modified to meet realistic boundary conditions for

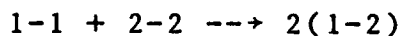
athermal mixing. By coupling the extended quasi-chemical theory with an arbitrary hard-body reference system, we obtain a new model for mixtures which can be applied to any equation of state of the van der Waals type. We outline here the derivation of this model and discuss how it meets desired boundary conditions for randomness and nonrandomness at high and low densities.

We discuss the general properties of the model which contains only two orthogonal binary parameters. It is too early to report on a definitive comparison between calculated and observed phase behavior because as yet, we do not have sufficient experience concerning how well the theory can fit experiment. With two adjustable binary parameters it is likely that the fit will be good but we must remember that this is no evidence for the theory's validity. A more meaningful test will be to compare the theory with molecular-dynamic calculations for representative systems.

#### EXTENDED QUASI-CHEMICAL THEORY

Fig. 1 shows an outline of the procedure used by Guggenheim (1935) to derive the Quasi-chemical Theory of liquid mixtures. Starting from an expression for the excess molar energy as a function of the number of 1-2 nearest neighbors and energy parameters  $\epsilon_{11}$ ,  $\epsilon_{22}$  and  $\epsilon_{12}$ , Guggenheim uses the Gibbs-Helmholtz relation to obtain the excess Helmholtz energy

of the mixture. To establish a relation between the number of 1-2 nearest neighbors and the energy parameters  $\epsilon_{ij}$ , Guggenheim considers a "quasi-chemical reaction"



for which the "equilibrium constant" is a function of the interchange energy  $w$  as shown in Fig. 2. We call this procedure Guggenheim's Ansatz.

Guggenheim's treatment is limited to liquid mixtures of spherical, equisized molecules. (A later modification of the original Quasi-chemical Theory was developed for mixtures of molecules consisting of segments of equisized spheres, which interact with each other by a spherically symmetrical intermolecular potential.) To make progress, we use two-fluid theory to bifurcate Guggenheim's Ansatz such that we obtain as independent variables the local mole fractions  $x_{12}$  and  $x_{21}$ , as indicated in Fig. 2.

For the calculation of the excess internal energy, we refer to an ideal solution of "ideal" hypothetical fluids (1) and (2), where the structure of the fluids is the same as that in the real solution, but where the energy interaction parameter between unlike molecules is given by the arithmetic mean as shown in Fig. 3. When we "flip" on the real forces by changing energy parameter  $\epsilon_{12}^0$  (ideal mixture) to  $\epsilon_{12}$  (real mixture), we obtain the real solution. This gives an expression



for the excess internal energy, which is essentially equal to the one usually used.

We propose to include an entropic contribution to nonrandomness, following Guggenheim's suggestion that the argument in the exponential should be a free-energy rather than an energy parameter. For mixtures of nonpolar molecules this entropic contribution, as shown in Fig. 4, accounts for both size and shape differences. For more complex mixtures, it accounts for molecular orientation (angular dependence) in the intermolecular potential of polar or hydrogen-bonding molecules.

The argument in our Boltzmann factors vanishes when the unlike-molecule interaction  $\epsilon_{12}$  is given by  $(\epsilon_{11} + \epsilon_{22})/2$ . The previously used argument  $\epsilon_{ij}$  (e.g. Wilson equation) overcorrects; it produces too much "order" in the mixture (Fischer, 1982).

#### EXCESS PROPERTIES AT HIGH DENSITIES

Fig. 5 shows the relation we obtain for the excess internal energy in the high-density limit. When the Boltzmann factor is small and the exponential is expanded in a series, the leading term is quadratic in "effective" size fractions  $\theta_i$  and goes to a van Laar form in first order for the simple case where the mixture contains only nonpolar molecules.

The expression for the excess internal energy shown in Fig. 5 meets the random-mixing boundary condition as  $w/kT$  goes to zero and fulfills the athermal mixing requirement when the interchange energy vanishes, regardless of entropy parameter  $r$ .

For an equimolar binary mixture of equisized molecules, Fig. 6 compares excess entropies and energies for the proposed model, the Quasi-chemical Theory of Guggenheim and the original two-fluid theory with expressions in the Boltzmann factors according to Wilson (1964). In the left diagram we see the increased order which is predicted by the original two-fluid theory. In the right diagram we see that the excess energy (according to Wilson) does not vanish when  $\epsilon_{12}=(\epsilon_{11}+ \epsilon_{22})/2$ .

#### EQUATION OF STATE FOR HIGHLY NONIDEAL MIXTURES

To obtain an equation of state for the entire fluid density range, our energy parameters must be density dependent. We can achieve that by first relating the energy parameter (per surface area) to a free energy parameter (per surface area) via the Gibbs-Helmholtz relation. Second, as shown in Fig. 7, the density-dependent free-energy parameter must vanish at zero density to obtain random mixing at low densities. Integration of the expression for the excess energy gives an equation for the excess Helmholtz energy (Fig. 7), where we split the free-energy parameters in the exponentials of the Boltz-

mann factors into an energetic and an entropic part.

We propose to use for the entropic contribution a function given in Fig. 8. For low densities, the entropic term goes to unity, satisfying the random mixing condition. The high-density limit is determined by binary parameter  $r$  which reflects difference in molecular size and shape for mixtures of nonpolar molecules and reflects molecular orientation and angular dependence of the intermolecular potential for mixtures containing polar or hydrogen-bonding molecules. The particular function shown in Fig. 8 meets desired boundary conditions but otherwise it is arbitrary.

Our method can be used to extend to mixtures any equation of state of the van der Waals type. Fig. 9 shows the general form of the resulting local-composition equation of state. The choice of the reference system is incorporated through the proper high-temperature integration constant required upon integrating the Gibbs-Helmholtz equation.

Fig. 10 shows the effective van der Waals constant for a binary mixture in reduced form. At low densities the non-randomness correction is negligible. More significant than the percent deviation from random mixing at high densities is the difference in the slopes, because these are directly related to the chemical potentials. For this highly asymmetric model mixture, changing the entropic parameter  $r$  from 1 to 2 drastically affects one of the limiting activity coefficients

while the other is not changed much.

Our calculations indicate that the "switch" parameter  $\lambda$  has no significant effect on the results. We expect  $\lambda$  to be a universal constant.

Fig.11 shows the general properties of the proposed equation of state for binary mixtures. This equation can readily be generalized to multicomponent mixtures using only two adjustable binary parameters per binary.

The proposed model offers an important advantage; it can be adapted to commonly-used working equations of state by incorporating first-order nonrandomness corrections, as shown in Fig. 12. All these energetic, entropic and (cross-term) energetic/entropic corrections are cubic in mole fraction. Also, they are at least quadratic in density, assuring that they don't influence the second virial coefficient.

### CONCLUSIONS

Our conclusions are shown in Fig. 13. There are two essential achievements. First, we have proposed a method for incorporation of entropic effects caused by differences in size and shape and angular dependence of the intermolecular potential. Second, we have so normalized the equations that there is random mixing and athermal mixing when  $\epsilon_{12}$  is given by the arithmetic mean  $(\epsilon_{11} + \epsilon_{22})/2$ .

The resulting model has two adjustable parameters per binary which are expected to be orthogonal because the physical significance of one is completely different from that of the other; one is energetic and the other is entropic.

Before we proceed to data reduction and prediction of phase behavior, further refinements are needed, especially in the functional dependence of the interchange entropy with temperature and density.

We shall welcome participation by other research groups concerning computer simulation to test crucial aspects of our extended Quasi-chemical Theory.

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# GUGGENHEIM'S QUASICHEMICAL THEORY FOR BINARY FLUID MIXTURES

1. GIBBS-HELMHOLTZ RELATION:

$$\frac{a^E}{T} = \left(\frac{a^E}{T}\right)_{1/T \rightarrow 0} + \int_0^{1/T} u^E d\left(\frac{1}{T}\right)$$

$a^E$  = excess molar Helmholtz energy  
 $u^E$  = excess molar energy

2. POSTULATE EXPRESSION FOR  $u^E$  AS A FUNCTION OF THE NUMBER OF THE 1-2 NEAREST NEIGHBORS  $zX$  ( $z$  = coordination number) AND ENERGY PARAMETERS  $\epsilon_{11}$ ,  $\epsilon_{22}$  AND  $\epsilon_{12}$

3. EXPRESS THE NUMBER OF NEAREST NEIGHBORS  $zX$  AS A FUNCTION OF  $w/kT$  WHERE INTERCHANGE ENERGY  $w = 2\epsilon_{12} - (\epsilon_{11} + \epsilon_{22})$  AND  $k$  = BOLTZMANN'S CONSTANT

HERE EXCESS (E) = IN EXCESS OF THAT GIVEN BY SOME  
REFERENCE SYSTEM

FIGURE 1

# LOCAL MOLE FRACTIONS FROM THE QUASICHEMICAL THEORY FOR BINARY FLUID MIXTURES OF EQUISIZED SPHERES

QUASICHEMICAL ANSATZ: 
$$\frac{X^2}{(N_1 - X)(N_2 - X)} = \exp - \frac{w}{kT}$$
  $N_i =$  number of molecules of component  $i$

DEFINING 
$$x_{21} = \frac{zX}{zN_1} \quad x_{12} = \frac{zX}{zN_2}$$
  $x_{ij} =$  local mole fraction of molecule  $i$  around molecule  $j$

WE OBTAIN 
$$\frac{x_{21} x_{12}}{x_{11} x_{22}} = \exp - \frac{w}{kT}$$

TO ALLOW  $x_{12}$  AND  $x_{21}$  TO BE INDEPENDENT VARIABLES, WE USE TWO-FLUID THEORY. THIS REQUIRES BIFURCATION OF GUGGENHEIM'S ANSATZ.

BIFURCATION HYPOTHESIS:

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \exp - \frac{w^{(1)}}{kT}$$

HYPOTHETICAL FLUID (1)

$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2} \exp - \frac{w^{(2)}}{kT}$$

HYPOTHETICAL FLUID (2)

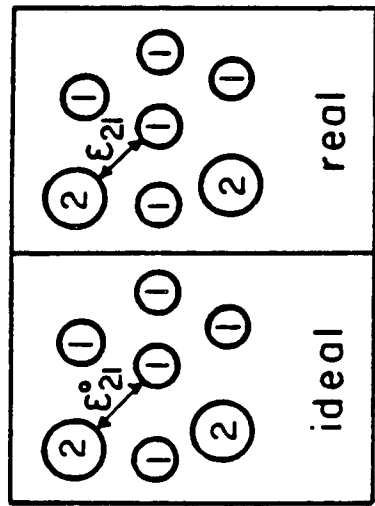
$x_i =$  bulk mole fraction of component  $i$

SUCH THAT  $w^{(1)} + w^{(2)} = w$

FIGURE 2

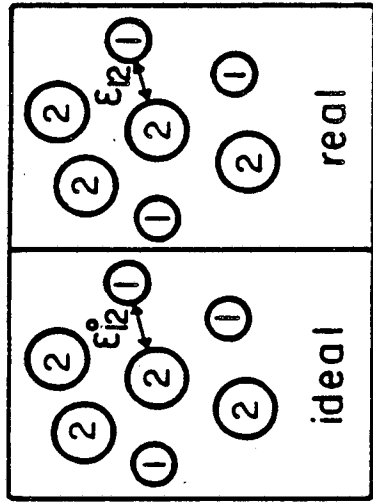


# TWO-FLUID THEORY FOR THE MOLAR INTERNAL ENERGY $u^M$ OF A BINARY MIXTURE USING LOCAL MOLE FRACTIONS



HYPOTHETICAL FLUID (1)

$$u^{(1)} = N_{AV} \frac{z}{2} q_1 (x_2 \epsilon_{21} + x_1 \epsilon_{11})$$



HYPOTHETICAL FLUID (2)

$$u^{(2)} = N_{AV} \frac{z}{2} q_2 (x_1 \epsilon_{12} + x_2 \epsilon_{22})$$

$$\epsilon_{12}^0 = \frac{1}{2} (\epsilon_{11} + \epsilon_{22})$$

FOR THE MIXTURE WE DEFINE  $u^E$ :

$$u^M = x_1 u_{real}^{(1)} + x_2 u_{real}^{(2)} = x_1 u_{ideal}^{(1)} + x_2 u_{ideal}^{(2)} + u^E$$

$$u^E = \frac{z}{2} N_{AV}^W \left\{ x_1 q_1 x_2 + x_2 q_2 x_1 \right\}$$

WE THEN FIND THAT

$$u^E = u^E(\text{usual}) + \text{smaller higher terms}$$

WHERE

$$u^E(\text{usual}) = u^M - x_1 u_{pure 1} - x_2 u_{pure 2}$$

$N_{AV}$  = Avogadro number

$\epsilon_{ij}$  = pair potential energy per surface area

$q_i$  = molecular size (or surface) parameter

$E$  = excess

FIGURE 3

IN LATER VERSIONS OF HIS WORK, GUGGENHEIM SUGGESTED THAT w SHOULD BE A FREE ENERGY PARAMETER

FOR BINARY FLUID MIXTURES OF RIGID MOLECULES OF DIFFERENT SIZE AND SHAPE, WE PROPOSE

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \exp \frac{\Delta^{(1)}}{k} \exp - \frac{w^{(1)}}{kT} \quad \text{HYPOTHETICAL FLUID (1)}$$

$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2} \exp \frac{\Delta^{(2)}}{k} \exp - \frac{w^{(2)}}{kT} \quad \text{HYPOTHETICAL FLUID (2)}$$

$\Delta$  = interchange entropy

WHERE  $w^{(i)}$  IS AN ENERGY (NOT A FREE ENERGY) PARAMETER:  $w^{(i)} = \epsilon_{ji} - \epsilon_{ji}^0$

FOR SIMPLE CASES,  $\exp \frac{\Delta^{(i)}}{k} = 1$  (e.g. mixtures of equisized spheres)

AT LIQUID-LIKE DENSITIES WE WANT AN EXPRESSION FOR  $u^E$  OF THE VAN LAAR FORM. THIS SUGGESTS (AT HIGH DENSITIES)

$$\exp \frac{\Delta^{(i)}}{k} = \exp - \frac{\Delta^{(j)}}{k} = r$$

FOR NONPOLAR MIXTURES, WE EXPECT

$$r = \frac{q_j}{q_i}$$

FIGURE 4

# EXCESS INTERNAL ENERGY OF A BINARY MIXTURE AT HIGH DENSITIES

EXPANDING THE EXPONENTIALS WHICH RELATE  $x_i$  TO  $x_{ij}$ ,

$$u^E = \frac{z}{2} N_{AV} (x_1 + x_2 r) \frac{q_1 + (q_2/r)}{2} \theta_1 \theta_2 \cdot w \left\{ 1 - \frac{1}{1 + \frac{x_1}{x_1 q_1 + x_2 q_2} (q_2/r) + \frac{x_2}{x_1 q_1 + x_2 q_2} q_1 r} \frac{w}{2kT} + \dots \right\}$$

WHERE

$$\theta_1 = \frac{x_1}{x_1 + x_2 r} \quad \text{and} \quad \theta_2 = \frac{x_2 r}{x_1 + x_2 r}$$

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FOR NONPOLAR MOLECULES  $r = \frac{q_2}{q_1}$  AND  $\theta_i$  IS A SURFACE (OR SIZE) FRACTION.  
THEN

$$u^E = \frac{z}{2} N_{AV} (x_1 q_1 + x_2 q_2) \theta_1 \theta_2 w \left\{ 1 - \frac{w}{4kT} + \dots \right\}$$

VAN LAAR

BOUNDARY CONDITIONS:

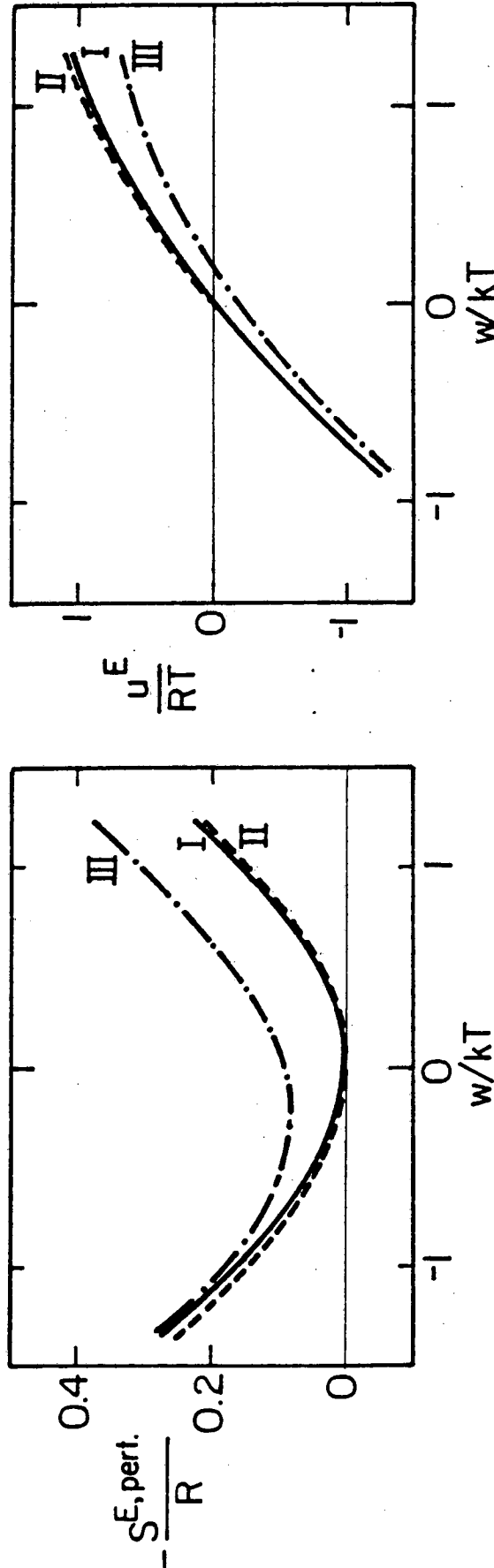
AS  $\frac{w}{kT} \rightarrow 0$ , MIXING IS RANDOM

AS  $w \rightarrow 0$ ,  $u^E \rightarrow 0$

FIGURE 5

SOME NUMERICAL RESULTS  
FOR SIMPLE BINARY MIXTURES AT HIGH DENSITIES

( $T = 300\text{ K}$ ;  $x_1 = x_2 = 0.5$ ;  $\epsilon_{22}/\epsilon_{11} = 2$ ;  $\epsilon_{12}/k = -350\text{ K}$ )



I = GUGGENHEIM'S ORIGINAL QC THEORY (NO BIFURCATION)

II = THIS WORK (BIFURCATION INCLUDED)

III = ORIGINAL TWO-FLUID THEORY (WILSON), WHERE

$$w^{(1)} = \epsilon_{21} - \epsilon_{11}, \quad w^{(2)} = \epsilon_{12} - \epsilon_{22} \quad \text{AND} \quad w = w^{(1)} + w^{(2)}$$

FIGURE 6

# EQUATION OF STATE FOR THE ENTIRE FLUID DENSITY RANGE

LET

$$\epsilon_{ij} = \left[ \frac{\partial(\eta_{ij}/T)}{\partial(1/T)} \right]_{\rho}$$

$\eta_{ij}$  depends on T and density  $\rho$ , such that

$$\eta_{ij} \rightarrow 0 \text{ as } \rho \rightarrow 0$$

SUPPOSE

$$\eta_{ij} \propto \rho$$

AS IN V.D.W. EQUATION

$$\eta = - \frac{a\rho}{(z/2)N_{AV}q}$$

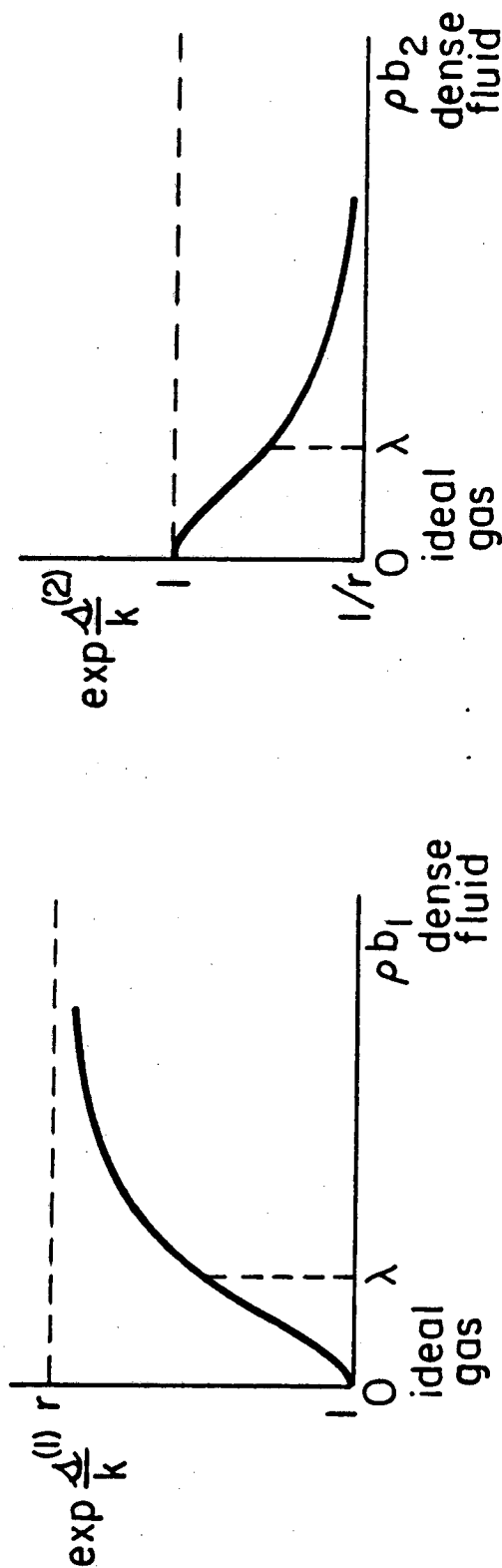
$$a = \text{v.d.W. "constant"} = f(T)$$

THEN

$$\frac{\partial E}{RT} = - \frac{z}{2} \left\{ x_1 q_1 \ln(x_1 + x_2 \exp \frac{\Delta^{(1)}}{k} \exp - \frac{w}{2kT}) + x_2 q_2 \ln(x_1 \exp \frac{\Delta^{(2)}}{k} \exp - \frac{w}{2kT} + x_2) \right\}$$

AT HIGH DENSITIES  $a^E$  IS SIMILAR TO WILSON'S EQUATION BUT THE ARGUMENT OF THE BOLZMANN FACTOR IS NOW  $\epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22})$  RATHER THAN  $(\epsilon_{21} - \epsilon_{11})$  OR  $(\epsilon_{12} - \epsilon_{22})$

# PROPOSED INTERPOLATION FUNCTION FOR $\Delta^{(i)}/k$



FOR NONPOLAR MIXTURES

$$r = \frac{q_2}{q_1}$$

$$\exp \frac{\Delta^{(1)}}{k} = (r-1) \frac{(\rho b_1)^2}{(\rho b_1)^2 + \lambda^2} + 1$$

$$\exp \frac{\Delta^{(2)}}{k} = \left(\frac{1}{r}-1\right) \frac{(\rho b_2)^2}{(\rho b_2)^2 + \lambda^2} + 1$$

$\rho$  = density

$b$  = van der Waals volume

$\lambda$  = reduced density that determines the point of inflection

FIGURE 8

EQUATION OF STATE FOR BINARY FLUID MIXTURES OF RIGID MOLECULES OF DIFFERENT SIZE AND SHAPE

$$Z = \frac{P}{\rho RT} = Z^{ref} + Z^{pert}$$

AS A REFERENCE WE USE A HARD-BODY EQUATION OF STATE (e.g. CARNAHAN-STARLING). IF WE ASSUME THAT FOR THE PERTURBATION WE CAN WRITE FOR A PURE FLUID:

$$Z^{pert} = - \frac{a\rho}{RT} \quad a = \text{van der Waals "constant"} = f(T)$$

THEN FOR A BINARY MIXTURE

$$Z^{pert} = \underbrace{x_1 Z_1^{pert} + x_2 Z_2^{pert}}_{\text{IDEAL MIXING}} + x_1 x_2 (Z_{12}^{pert} + Z_{21}^{pert})$$

WHERE

$$Z_{ij}^{pert} = - \frac{\rho}{RT} q_j \frac{\Lambda_{ij}}{x_j + x_i \Lambda_{ij}} N_{AV} \left[ \frac{\partial w/2}{\partial \rho} - T \frac{\partial s^{(j)}}{\partial \rho} \right]$$

$$\Lambda_{ij} = \left[ \exp \frac{\Delta_{ij}}{k} \right] \left[ \exp - \frac{w}{2kT} \right]$$

$$w/2 = \epsilon_{ij} - \epsilon_{ij}^0$$

COMBINING RULES:

$$\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{1/2} (1 - k_{ij})$$

$$\epsilon_{ij}^0 = \frac{1}{2} (\epsilon_{ii} + \epsilon_{jj})$$

$$\epsilon_{ii} = \frac{2}{z} \frac{\rho}{N_{AV}} \left[ \frac{\partial}{\partial (1/T)} \left( - \frac{a_{ii}}{q_i T} \right) \right] \rho$$

FIGURE 9

EFFECTIVE VAN DER WAALS CONSTANT  $a_M$   
FOR A BINARY MIXTURE

$(\frac{a_{22}}{a_{11}} = 3; T = 273 K; k_{12} = 0.07)$

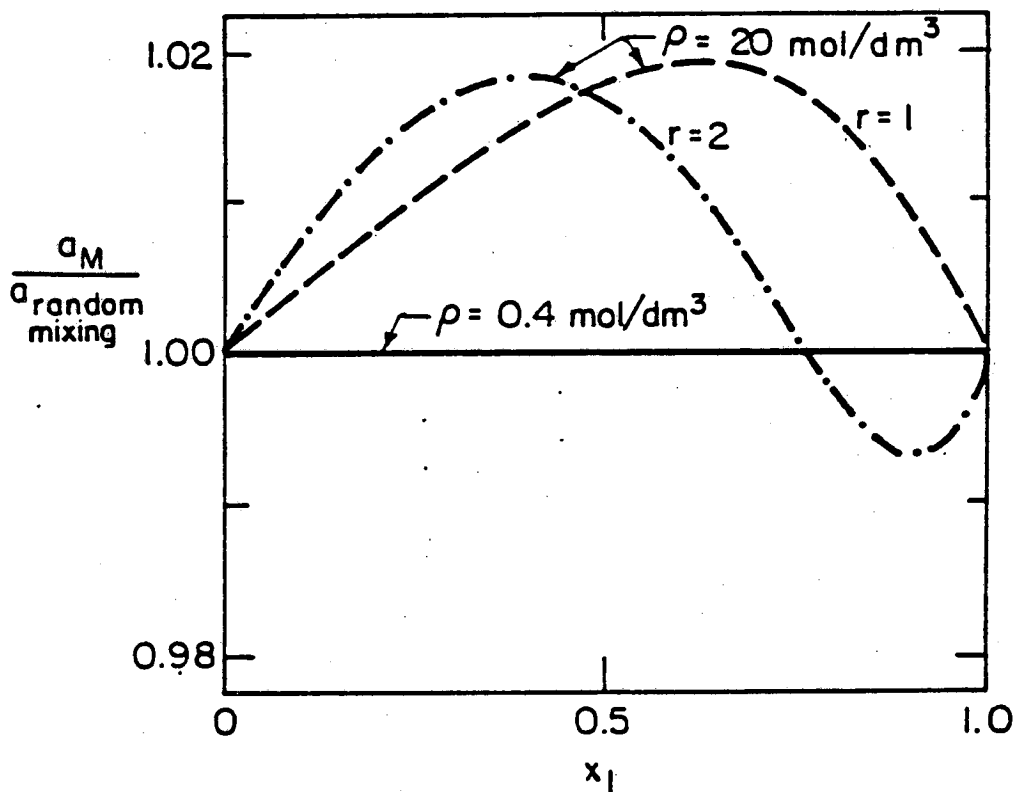


FIGURE 10



# PROPERTIES OF EQUATION OF STATE FOR MULTICOMPONENT MIXTURES

AT LOW DENSITIES (AS  $\rho \rightarrow 0$ )

$$P \rightarrow \rho RT$$

$$\frac{x_{ij}}{x_{jj}} \rightarrow \frac{x_i}{x_j} \quad (\text{RANDOM MIXING})$$

SECOND VIRIAL COEFFICIENT:

$$B_M = \sum_i \sum_j x_i x_j B_{ij}$$

AT HIGH DENSITIES (AS  $\rho \rightarrow \rho_{\text{LIQUID}}$ )

$$\frac{x_{ij}}{x_{jj}} \rightarrow \frac{\theta_i}{\theta_j} \exp - \frac{w(i)}{kT}$$

FOR  $w = 0$ ,  $s^E$  DEPENDS ON CHOICE OF  $\left(\frac{\rho^E}{T}\right)_{T \rightarrow 0}$  AND REFERENCE SYSTEM.

FOR EXAMPLE, WE CAN OBTAIN

$\Delta S_{\text{mixing}} \rightarrow$  FLORY-HUGGINS ENTROPY OF MIXING

FIGURE 11

## FOR PRACTICAL APPLICATIONS, EXPAND EXPONENTIALS IN A TAYLOR SERIES

SUPPOSE

$$Z^M = Z^{\text{ref}} - \frac{\partial \rho}{RT}$$

THEN FOR A BINARY MIXTURE

$$Z^M = Z^{\text{CONVENTIONAL}} + \underbrace{(Z^M)_{\text{U}}^{\text{corr}} + (Z^M)_{\text{S}}^{\text{corr}} + (Z^M)_{\text{US}}^{\text{corr}} + \dots}_{\text{1st order correction terms}}$$

WHERE

$$(Z^M)_{\text{U}}^{\text{corr}} = -\frac{Z}{2} N_{\text{AV}}^2 \frac{\rho}{RT} \sum_{i=1}^2 x_i \sum_{j=1}^2 x_i x_j q_i \frac{\epsilon_{ji} - \epsilon_{ji}^0}{RT} \left[ \frac{\partial (\epsilon_{ji} - \epsilon_{ji}^0)}{\partial \rho} \right]$$

$$(Z^M)_{\text{S}}^{\text{corr}} = -\frac{Z}{2} N_{\text{AV}}^2 \frac{\rho}{RT} T \sum_{i=1}^2 x_i \sum_{j=1}^2 x_i x_j q_i (1 - \delta_{ij}) \frac{\Delta^{(i)}}{R} \left( \frac{\partial \Delta^{(i)}}{\partial \rho} \right)_T \quad \delta_{ij} = \text{Kronecker delta}$$

$$(Z^M)_{\text{US}}^{\text{corr}} = \frac{Z}{2} N_{\text{AV}}^2 \frac{\rho}{RT} \sum_{i=1}^2 x_i \sum_{j=1}^2 x_i x_j q_i \left\{ \frac{\Delta^{(i)}}{R} \left[ \frac{\partial (\epsilon_{ji} - \epsilon_{ji}^0)}{\partial \rho} \right]_T + \left( \frac{\partial \Delta^{(i)}}{\partial \rho} \right)_T \frac{\epsilon_{ji} - \epsilon_{ji}^0}{R} \right\}$$

- FOR MANY MIXTURES, THE CONVENTIONAL MODEL IS SUFFICIENT BUT FOR STRONGLY NONIDEAL MIXTURES IT MAY BE WORTHWHILE TO INCLUDE NONRANDOMNESS CORRECTIONS AS INDICATED ABOVE.
- CORRECTIONS DO NOT INFLUENCE THE SECOND VIRIAL COEFFICIENT.
- CORRECTIONS VANISH WHEN  $\epsilon_{ij} = \epsilon_{ij}^0$  AND  $r = 1$ .

## CONCLUSIONS

1. THE QUASI-CHEMICAL THEORY HAS BEEN EXTENDED WITHIN THE FRAMEWORK OF TWO-FLUID THEORY BY AN ENTROPIC CONTRIBUTION TO NONRANDOMNESS.
2. THE RESULTING EXPRESSION FOR THE EXCESS ENERGY IS OF THE VAN LAAR TYPE IN FIRST ORDER WHEN THE ENTROPY PARAMETER  $r = q_2/q_1$ . ATHERMAL MIXING IS OBTAINED WHEN ENERGY PARAMETER  $\epsilon_{12} = 1/2 (\epsilon_{11} + \epsilon_{22})$ .
3. COUPLED WITH A SUITABLE HARD-BODY REFERENCE SYSTEM, AN EQUATION OF STATE FOR HIGHLY NONIDEAL FLUID MIXTURES IS OBTAINED.
  - a. IDEAL GAS AS DENSITY  $\rho \rightarrow 0$
  - b. RANDOM MIXING AT LOW DENSITIES
  - c. SECOND VIRIAL COEFFICIENT QUADRATIC IN MOLE FRACTION
  - d. AT HIGH DENSITIES, FLORY-HUGGINS ENTROPY OF MIXING CAN BE OBTAINED
  - e. EXTENSION TO MULTICOMPONENT MIXTURES IS STRAIGHTFORWARD. ONLY TWO BINARY PARAMETERS ARE REQUIRED PER BINARY, ONE ENERGETIC AND ONE ENTROPIC
4. MODEL CAN BE ADAPTED TO THE COMMON WORKING EOS (SRK, PR etc.) BY INCLUDING APPROPRIATE FIRST-ORDER CORRECTION TERMS

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