CHEMPOR'85

4th INTERNATIONAL CHEMICAL ENGINEERING CONFERENCE

University of Coimbra

Coimbra — Portugal

April 15-19, 1985

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4.ª CONFERÊNCIA INTERNACIONAL DE ENGENHARIA QUÍMICA

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SCIENTIFIC PROGRAMME

BLOCK 1 - <u>THERMOPHYSICAL PROPERTIES</u>

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Jorge C.G. Calado (Cornell, USA, and T. Lisboa, PORTUGAL)

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K.E. Gubbins (Cornell, USA)

02 *Prediction of VLE Data for Two-Component Mixtures from Heats of Mixing and the Complete Local Concentration Model*
N. Chiou and D. Yarbrough (Tennessee, USA)

03 *Prediction of VLE and LLE by the ASOG Method*
A. Arce, A. Blanco, J.M. Correa, M.R. Mendez and J. Tojo (Santiago and Vigo, SPAIN)

04 *Some Difficulties on the Application of the UNIFAC Model for the Prediction of LLE Compositions*
M.G. Bernardo Gil and L.J.S. Soares (Lisboa and Minho, PORTU̲ GAL)

05 *VLE of Polar Mixtures: A New Generalised Correlation*
S. Persio Ravagnani and S.G. d'Ávila (Campinas, BRASIL)

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Y. Adachi and B.C.-Y. Lu (Ottawa, CANADA)

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T.R. Kubendran, M.R.V. Krishnan and G.S. Laddha (Anna/ Madras, INDIA)

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     J.P. Petitet, L. Denielou, R. Tufeu and B. LeNeindre (Paris, FRANCE)

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COMPUTER SIMULATION AND THEORETICAL STUDIES OF LIQUID MIXTURES:
BRUTE FORCE vs. INSIGHT

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ABSTRACT

Recent advances in our understanding of the thermodynamics of molecularly simple liquid mixtures based on theory and computer simulation are reviewed. Perturbation theories based on spherical and nonspherical reference fluids are described, and examples are given of comparisons with experiment. Computer simulation studies of model fluid mixtures in which the molecules possess both nonspherical shape and electrostatic forces are proving useful in understanding the role of these molecular effects in thermodynamics, and are briefly discussed. Finally, a summary is given of recent work on the vapour-liquid interface for simple mixtures.

INTRODUCTION

The thermodynamic properties of mixtures can be studied by experiment, theory, or computer simulation (Fig. 1). In this review only the last two methods will be covered, with the emphasis on (a) comparison of theoretical and simulation results, and (b) comparison of theory and experiment. The discussion will focus on molecularly simple mixtures, e.g. the inert gases, CH_4, CH_3OH, CO_2, HCl, etc. We shall not deal specifically with ionic fluids (electrolytes, fused salts, etc.), aqueous solutions or polymers.

For the thermodynamic properties, perturbation theory provides the most convenient compromise between rigour and ease of calculation at present. A survey of the existing theories is given in Section 2, with the emphasis on molecular rather than atomic fluids. These theories can be conveniently divided into those based on a reference fluid of spherical molecules, and those based on a reference of nonspherical molecules. The former are easier to use, but do not work well for strong orientation-dependent forces. The latter work better, but are more difficult to use. Most comparisons with experiment have so far been for the simpler spherical reference theories. Some examples of such comparisons are given in Section 3. Both the electrostatic and induction forces have a large effect on the thermodynamic properties. Comparatively few computer simulation studies have been reported so far on mixtures of simple model nonspherical molecules. This area is reviewed in Section 4, and results for models in which the molecules

have nonspherical shape (spherocylinders, dumbells, etc.) and/or electrostatic forces are summarized. Finally, in Section 5 some recent results for the vapour-liquid interface of spherical Lennard-Jones mixtures are discussed.

PERTURBATION THEORY

In perturbation theory the Helmholtz free energy A for the fluid mixture of interest is expanded about the value A_0 for some reference fluid in which the intermolecular potential energy is U_0. The expansion is carried out in terms of the perturbation potential $U_p \equiv U-U_0$, where U is the intermolecular potential energy of the full system; the parameterization method varies with the particular theory used. For spherical molecules such perturbation theories are well established; for reviews see, for example, McDonald (1973), Smith (1973) and Gubbins et al. (1983). Of particular value are the Weeks-Chandler-Anderson (WCA) form of hard sphere perturbation theory and the van der Waals 1-fluid (vdW1) form of conformal solution theory. We do not dwell on these theories here, but shall focus our attention on theories for nonspherical molecules. For a more detailed review of these theories see Gray and Gubbins (1984).

Spherical Reference Molecules

Three different choices of spherical reference potentials have been suggested; we refer to these theories as the u-expansion, f-expansion, and

median potential theory. The median potential theory (see, e.g. MacGowan et al., 1984) fails for electrostatic forces, and we do not describe it further here.

The u-Expansion. This is the oldest of the perturbation theories for molecular fluids, and is the easiest to use. The reference pair potential $u_0(r)$ is defined by

$$u_0(r) \equiv \langle u(r\omega_1\omega_2)\rangle_{\omega_1\omega_2} \qquad (1)$$

where $u(r\omega_1\omega_1)$ is the full pair potential for the fluid of interest, ω_i is the orientation of molecule i ($\theta_i\phi_i$ for linear or $\theta_i\phi_i\chi_i$ for nonlinear molecules), and $\langle\cdots\rangle_{\omega_1\omega_2}$ means an unweighted average over molecular orientations. With this choice the first-order perturbation term A_1 vanishes and the series for the Helmholtz energy becomes

$$A = A_0 + A_2 + A_3 + \ldots \qquad (2)$$

The second-order term A_2 involves integrals over the two- and three-body reference correlation functions. The third-order term A_3 is more complex in general, but for electrostatic forces reduces to integrals over two- and three-body reference correlation functions. These integrals have been evaluated and fitted to simple functions for a variety of intermolecular force types (Gubbins and Twu, 1978; Nicolas et al., 1979),

and detailed descriptions of the theory and its use have been given by Gubbins and Twu (1978), Twu and Gubbins (1978), and Moser et al. (1981).

Unfortunately, the series of eqn. (2) is slow to converge, and even the inclusion of A_3 is not sufficient to deal with strongly polar molecules such as alcohols or water. This led Stell et al. (1974) to propose a Padé approximant to the series,

$$A = A_0 + A_2/(1 - A_3/A_2) \qquad (3)$$

This equation agrees well with computer simulation results for fluids with strong electrostatic forces, provided that the molecules possess spherical or near spherical cores. Typical results are shown in Fig. 2. Recently this theory has been extended to include quantum corrections (Clancy and Gubbins, 1981), nonaxial molecules (Gubbins et al., 1981) and induction effects (Wertheim, 1979; Venkatasubramanian et al., 1984).

The u-expansion is convenient and gives a good account of the effects of electrostatic forces on thermodynamic properties. It is much less satisfactory for molecules with highly nonspherical cores or for describing fluid structure.

The f-Expansion. In this expansion, also called the RAM (reference average Mayer function)

theory, the reference potential $u_0(r)$ is defined through an unweighted average over orientations of the Boltzmann factor $\exp[-u(r\omega_1\omega_2)/kT]$,

$$\exp[-u_0(r)/kT] = \langle\exp[-u(r\omega_1\omega_2)/kT]\rangle_{\omega_1\omega_2} \qquad (4)$$

This reference potential includes an averaged contribution from the anisotropic part of the potential, and also gives the second virial coefficient exactly. Thus, the zeroth order f-expansion becomes exact in the low density limit. However, the potential $u_0(r)$ depends on temperature and must be calculated numerically for each new temperature or intermolecular potential function. Thus the f-expansion is less convenient to use than the u-expansion.

With this choice of reference the A_1 term again vanishes and the free energy series is again given by eqn. (2). Terms beyond A_2 have not been calculated. The fluid structure is usually obtained by expanding the pair function $y(r\omega_1\omega_2) \equiv \exp[u(r\omega_1\omega_2)/kT]g(r\omega_1\omega_2)$, i.e.

$$g_f(12) = \exp[-u(12)/kT] \left[y_0(r) + y_1(12) + \ldots\right] \qquad (5)$$

where $y(12) \equiv y(r\omega_1\omega_2)$, etc. Here $g(r\omega_1\omega_2)$ is the pair correlation function. The fluid structure calculated from the f-expansion is generally

better than from the u-expansion, though there are still considerable discrepancies. The structure results can be improved somewhat by using the 'reduced form' of the theory (Smith and Nezbeda, 1981, 1983), in which the pair correlation function is given by

$$g(12) = \frac{g_f(12)}{g_{f,000}(r)} g_0(r) \qquad (6)$$

where the f-expansion is used to calculate the ratio $g_f(12)/g_{f,000}(r)$, where $g_f(12)$ is given by eqn. (5) and $g_{f,000}(r)$ is the $\ell\ell'm = 000$ spherical harmonic co-efficient of $g(12)$, defined in general by

$$g_{\ell\ell'm}(r) = 4\pi <g(12) \, Y_{\ell m}(\omega_1')^* \, Y_{\ell'\underline{m}}(\omega_2')^*>_{\omega_1'\omega_2'} \qquad (7)$$

where $Y_{\ell m}$ is the spherical harmonic in the convention of Rose (1957), ω_i' is the orientation of molecule i in the intermolecular frame, and $\underline{m} \equiv -m$. The reference pair correlation function $g_0(r)$ that appears in eqn. (6) is calculated from the Percus-Yevick theory.

In Fig. 3 the f-expansion results are compared with simulation data for the structure of two simple model fluids, the hard dumbell (HD), a simple model of nonspherical shape, and the hard dumbell plus point charge quadrupole (HD+PCQ), a

model in which the molecules also possess strong electrostatic forces. The three harmonic coefficients of g(12) shown are those that are most important for the thermodynamic properties. For the HD fluid the first-order theory gives good results for g_{220} and g_{221}, but is poor for g_{222}. For the HD+PCQ fluid the theory gives rather poor results for all three harmonics, and the first-order theory is no better than zeroth order. The pair correlation function for molecular centres, g(r), is given quite accurately by the theory for these fluids (Wojcik and Gubbins, 1984b).

The results of the reduced form of the theory for the free energy are shown in Fig. 4 for the HD+PCQ fluid. The theory overestimates the electrostatic contribution to the free energy.

Nonspherical Reference Potentials
From the previous section it will have become clear that theories based on spherical reference molecules are unsatisfactory, particularly for fluids of molecules that are nonspherical in shape and also exert electrostatic forces. Most recent work in perturbation theory has been aimed at finding suitable reference fluids of nonspherical molecules. Expansions about such a fluid should be more rapidly convergent, but usually at the cost of added complexity. Reference fluids of hard, nonspherical molecules such as dumbells or spherocylinders are often used, as accurate equations are now known for the thermodynamic

properties of such fluids.

Nonspherical reference perturbation theories can be conveniently divided into two types: (a) those that divide the full pair potential $u(\underline{r}\omega_1\omega_2)$ into two parts, usually a repulsive and an attractive branch as in Weeks-Chandler-Andersen (WCA) theory for spherical molecules; this splitting is, of course, different for different molecular orientations; and (b) those that are restricted to interaction site model (ISM) potentials, where the full potential is the sum of site-site potentials $u_{\alpha\beta}(r)$ between molecular sites α and β, and where $u_{\alpha\beta}$ is divided, usually into repulsive and attractive branches. In both approaches the reference fluid properties are usually related to those of a fluid of hard molecules, e.g. dumbells. In the theories of type (a) the reference fluid pair correlation function $g_0(\underline{r}\omega_1\omega_2)$ is unknown, and must be estimated. This is often estimated using the f-expansion. This approach has been applied to fluids of two-centre Lennard-Jones (Kohler et al., 1979; Fischer, 1980; Quirke and Tildesley, 1983) and Gaussian overlap (Monson and Gubbins, 1983) molecules. The principal weakness in theories of this type is in the evaluation of the reference correlation function. An interesting variant of this theory is due to Boublik and his collaborators (Boublik, 1974, 1976, 1979, 1981; Pavlicek and Boublik, 1981),

who apply it to fluids in which the molecules obey a Kihara potential. In this model the molecules contain a hard convex core, and the intermolecular potential depends on the shortest distance $\rho = \rho(r\omega_1\omega_2)$ between molecular cores, rather than on the distance between molecular centres. The perturbation terms can then be simplified using the geometry of hard convex bodies, and it is found that A_1 involves only the correlation function $g_0(\rho)$ rather than the full pair correlation function $g_0(r\omega_1\omega_2)$. Here $g_0(\rho)$ is proportional to the probability that a molecular pair has a minimum distance ρ between cores. The accuracy of this theory has not yet been tested against computer simulation results, primarily because simulations of Kihara fluids would be very time consuming.

Theories of type (b) for ISM fluids have the advantage that one only needs to know the site-site correlation functions $g_0^{\alpha\beta}(r)$ for the reference fluid and not the full pair correlation function. Such theories have been proposed by Chandler and Andersen (1972), Tildesley (1980), Lombardero et al. (1981a), and Enciso and Lombardero (1981). The site-site correlation functions can be calculated using the reference interaction site model (RISM) theory of Chandler and Andersen (1972) or related theories. The theory gives good reults for ISM fluids in the absence of electrostatic forces for both thermodynamics and structure (Tildesley, 1980).

The theories described above have for the most part been applied to either molecules having spherical shape plus electrostatic forces, or to molecules with nonspherical shape but no electrostatic forces. Real molecules usually have nonspherical shape _and_ electrostatic forces, and the theories are usually poorer for such cases. To illustrate this we consider a fluid of hard dumbells in which the molecules have embedded point charges arranged in a quadrupolar symmetry, i.e. positive charges q on each of the sphere centres, and a negative charge -2q at the molecular centre. We call this the HD+PCQ model. One obvious reference fluid is one of hard dumbells in the absence of point charges, so that the free energy series is

$$A = A_{HD} + A_1 + A_2 + A_3 + \ldots \qquad (8)$$

However, this reference system does not contain all the strong short-range forces, nor even all the repulsive forces, since the electrostatic forces will have repulsive regions for certain molecular orientations. If we include the repulsive part of the electrostatic forces in the reference potential, in addition to the HD part, eqn. (8) is modified to

$$A = A_{REP} + A_1 + A_2 + \ldots \qquad (9)$$

where A_{REP} is the free energy of the repulsive

force reference fluid. These two series have been recently studied by Wojcik and Gubbins (1984b) using Monte Carlo simulations in which the various terms A_{HD}, A_{REP}, A_1, and A_2 are evaluated exactly. The results are shown in Fig. 4. The HD reference system gives especially poor results; the A_1 term alone greatly underestimates the electrotatic forces, while the inclusion of A_2 overestimates it. The REP reference system gives better results. The A_1 term alone still underestimates the effect of electrostatic forces, but the inclusion of A_2 now gives results that agree almost exactly with the Monte Carlo values for A. This series appears to warrant further study, although it is possible that yet better reference fluids may be found by including part of the strong attractive forces in the reference potential. The structure results for the REP fluid are intermediate between those for the HD and HD+PCQ fluids (Wojcik and Gubbins, 1984b).

Although the series of eqn. (8) is poorly convergent, it is possible that a Padé approximant to the series might give good results, as in the case of the u-expansion. Rasaiah et al. (1975) and Martina et al. (1979, 1981) have suggested the Padé

$$A = A_{HD} + A_1 + A_2/(1 - A_3/A_2) \qquad (10)$$

To avoid the difficulty of calculating the HD correlation functions that appear in A_2 and A_3