

## Mixtures of polar and associating molecules

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**Abstract** - Recent advances in the statistical thermodynamics of polar liquid mixtures are reviewed. Perturbation theories are now available that successfully describe the effects of both direct electrostatic and induction forces, provided the molecules are not too nonspherical in shape. New theories are also available for mixtures in which molecular association, solvation, or hydrogen bonding occurs, and initial comparisons with computer simulation results are encouraging. More accurate intermolecular potential models are needed in order to use these theories to predict the behavior of real polar liquids.

### INTRODUCTION

Thermodynamic nonideality in mixtures arises from differences in the intermolecular forces among the various molecular species present. These differences occur because of differences in molecular size, dispersion forces, molecular shape, polarity, polarizability, etc. For mixtures of neutral, spherical molecules the WCA form of perturbation theory gives a good account of nonidealities that arise from size and dispersion force differences (for reviews of this work see, for example, refs. 1-3). For mixtures of nonspherical molecules, somewhat different approaches have been used to describe effects due to nonspherical shape on the one hand, and effects due to polarity and polarizability on the other hand. For the first class of mixtures, in which the molecular species are nonpolar but differ in shape and dispersion forces, the liquid structure is largely determined by the repulsive forces (as is the case for neutral, spherical molecules), and the WCA approach is again quite successful. The reference fluid is one in which the molecules interact with the repulsive branch of the pair potential (or of the site-site potential in the case of interaction site models), and the attractive part of the potential is treated as a perturbation. This approach has been extensively applied to nonpolar liquids, and is described in several reviews (refs. 3-6) as well as in recent papers (e.g. refs. 7,8).

In this paper we focus our attention on the second class of mixtures, where polarity and polarizability play a significant role. In such liquids the structure is strongly influenced by the electrostatic, as well as the repulsive, forces and a simple WCA treatment is usually inadequate. If the molecules are not highly polar, and the dipole is not very much off-center it is usually possible to use perturbation theory to describe the thermodynamic properties. We describe this work in Section 2 below, and refer to such liquids as non-associating since the intermolecular interactions are relatively weak. When the electrostatic forces are strong, or off-center charge centers are important, the interactions are often much stronger, and long-lived dimers or higher *s*-mers can form. We refer to such cases as associated mixtures; the association can occur between like or unlike molecules, or both. Simple perturbation theory fails in such cases, and the most successful theories at present are based on cluster expansions. These are described in Section 3. It should be kept in mind that the distinction between non-associating and associating mixtures is quite arbitrary - in reality there is a continuous transition between the two types. The distinction is useful as a qualitative measure of the interaction strength, and also because the two classes of mixture are treated by different theories at present.

### MIXTURES WITH WEAK INTERACTIONS (NON-ASSOCIATING MOLECULES)

If the electrostatic interactions are not very strong or off-center, it is usually possible to describe the thermodynamic properties using perturbation theory. The usual expansion functional is either the intermolecular potential energy  $u$  itself (the *u*-expansion) or the Boltzmann factor  $\exp(-u/kT)$  (called the *f*-expansion or reference averaged Mayer function theory). In either case, the simplest theory is obtained when a reference fluid of spherical molecules is chosen. In this section we give a brief survey of these theories, and examples of their application to mixtures. More detailed reviews are given elsewhere (refs. 3-5).

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

$$u_o(r) \equiv \langle u(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} \quad (1)$$

where  $u(r\omega_1\omega_2)$  is the full pair potential for the fluid of interest,  $\omega_i$  is the orientation of molecule  $i$  ( $\theta_i\phi_i$  for linear or  $\theta_i\phi_i\chi_i$  for nonlinear molecules), and  $\langle \dots \rangle_{\omega_1\omega_2}$  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

$$A = A_o + A_2 + A_3 + \dots \quad (2)$$

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 (refs. 9,10), and detailed descriptions of the theory and its use have been given by Gubbins and Twu (ref. 9), Twu and Gubbins (ref. 11), and Moser *et al.* (ref. 12).

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.* (ref. 13) to propose a Padé approximant to the series,

$$A = A_o + A_2/(1 - A_3/A_2) \quad (3)$$

This equation agrees well with computer simulation results for fluids with strong electrostatic forces, provided that the molecules possess spherical or nearly spherical cores (ref. 4). This theory has been extended to include quantum corrections (ref. 14), nonaxial molecules (ref. 15) and induction effects (refs. 16,17).

Extensive comparisons of eqn. (3) with experimental data have been made. These comparisons have been for small, rigid molecules such as  $N_2$ , HBr, HCl, CO,  $N_2O$ ,  $C_2H_4$ ,  $CH_4$ ,  $CH_3Cl$ , etc. and have been reviewed recently (refs. 3,5,18). In Fig. 1 is shown an example taken from the work of Lucas (ref. 19). In these calculations the author fit potential parameters for the pure components, but not for the mixture; the mixture parameters are obtained from combining rules, and no fitting to mixture data is involved. Thus the comparison with experiment is a test of the theory's ability to describe the composition dependence. It is seen that the Padé gives much better results than the van der Waals 1-fluid theory or Redlich-Kwong equation, which assume the molecules to be spherical. This is because the Padé correctly accounts for the dipolar and quadrupolar forces that are present for HCl. Winkelmann (ref. 20) has applied the theory to mixtures involving acetone, diethyl ether, chloroform, dimethyl formamide, water, and methanol with good results. He fits an unlike pair potential parameter to mixture data, in addition to fitting parameters to pure fluid data. An example of his results is given in the vapour-liquid equilibrium plot of Fig. 2.

The  $u$ -expansion has been extended to include the effects of many-body induction forces (Fig. 3), which have been found to be important in polar liquids (refs. 16,23). Such effects are difficult to account for in conventional perturbation theory, but Wertheim (ref. 16) has proposed a graphical resummation method that he calls renormalization theory which results in an expression for the free energy that is similar in form to the Padé approximant of eqn. (3). The basic idea of the Wertheim approach is that most molecules in the liquid will have a dipole moment much closer to the average total, or renormalized, dipole moment  $\mu'$ , given by

$$\mu' = \mu + \alpha \cdot E' \quad (4)$$

where  $\mu$  is the permanent dipole moment,  $\alpha$  the polarizability, and  $E'$  the mean electric field experienced by the molecule in some fixed orientation  $\omega$ . Typically  $\mu'$  exceeds  $\mu$  by 20-30%, and occasionally by 100% or more. In Wertheim's renormalized theory one generates a perturbation expansion in terms of  $\mu'$  and  $\alpha$  rather than in  $\mu$  and  $\alpha$ . He calls this the 1-R theory (first level of renormalization). He also presents a 2-R theory in which  $\alpha$  is also renormalized to  $\alpha'$ . However, the 2-R theory usually gives results only slightly different from the 1-R theory. The theory is in good agreement with computer simulation results. Wertheim's renormalization theory has been extended to mixtures of purely polar fluids by Venkatasubramanian *et al.* (ref. 17), and to mixtures of quadrupolar molecules at both the 1-R (refs. 24,25) and 2-R (ref. 26) levels of renormalization. Calculations have been carried out for a wide variety of mixtures, and the renormalization theory has been compared with the un-renormalized (0-R) theory (which neglects many-body effects) and with experimental data. For the excess properties, the polarizability contribution is found to be of the order of 50% of the total in many cases. While the 1-R theory generally gives a much better account of such effects than the 0-R theory, the numerical differences between the 1-R and 2-R treatments are usually small. Some typical results for HCl/HBr mixtures are shown in Figs. 4 and 5, taken from the work of Gray *et al.* (ref. 25). The

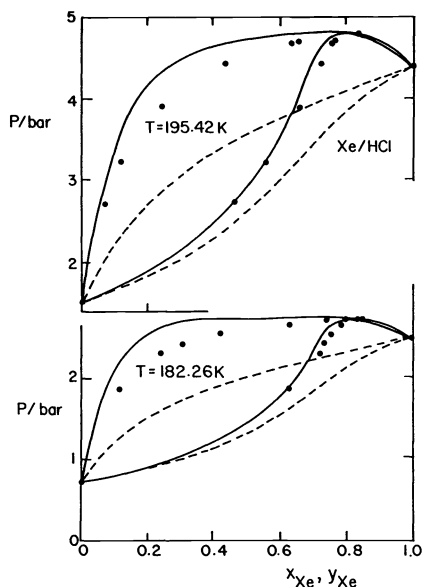


Fig. 1. Comparison of theory and experimental vapour-liquid equilibria for Xe/HCl mixtures. The experimental data (points) is from Calado et al.(ref.21). Solid lines are the results from the Padé approximant of eqn. (3) with Kohler (ref.22) combining rules, dashed lines are from the Redlich-Kwong empirical equation of state. The vdW1 theory gives results that are indistinguishable from those for the Redlich-Kwong equation on the scale of the plot.(From Lucas, ref.19.)

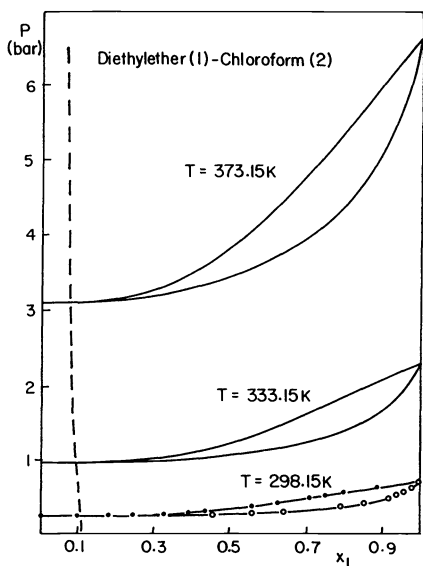


Fig. 2. Pxy results for chloroform-diethyl ether mixtures from experiment (points) and from eqn. (3), solid lines. Dashed line is azeotropic locus. (From Winkelmann, ref.20.)

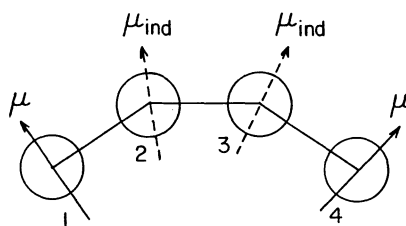


Fig. 3. A four-body induction term in the potential energy which arises from two permanent dipoles 1 and 4 interacting via dipoles induced in molecules 2 and 3.

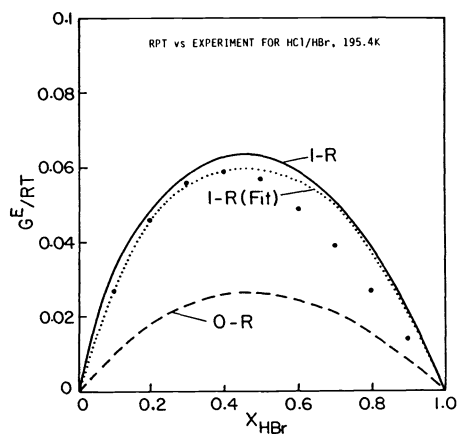


Fig. 4. GE for HCl/HBr mixtures at 195.4K, 0 bar. Experimental data (points) is from Calado et al.(ref. 21) and lines are theoretical calculations. (From Gray et al., ref. 25.)

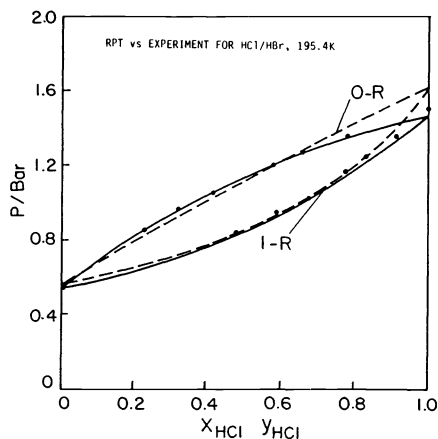


Fig. 5. Vapour-liquid equilibria for HCl/HBr at 195.4K. The 1-R and 1-R (Fit) results are almost indistinguishable on the scale of the plot. Key as in Fig. 4.

potential models for HCl and HBr consisted of a spherical Lennard-Jones term with the addition of dipole-dipole, dipole-quadrupole and quadrupole-quadrupole terms. Pure component Lennard-Jones parameters were obtained by fitting the theory to experimental vapour pressure and density data for the pure orthobaric liquid. In the results labelled 0-R and 1-R the unlike pair parameters  $\sigma_{\alpha\beta}$  and  $\epsilon_{\alpha\beta}$  were calculated from the Lorentz-Berthelot combining rules, while in the curve labelled 1-R(Fit)  $\epsilon_{\alpha\beta}$  was fitted to the value of the equimolar excess Gibbs energy. Dipole and quadrupole moments and polarizabilities were taken from the literature (ref. 4). The large difference between the 0-R and 1-R results for  $G^E$  is typical, and arises from neglect of multibody induction terms in the 0-R theory.

The u-expansion described above 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 is an attempt to overcome these defects to some extent, while retaining the simplicity of a reference fluid of spherical molecules. In this theory the reference potential is defined through an unweighted average over orientations of the Boltzmann factor  $\exp[-u(r\omega_1\omega_2)/kT]$ ,

$$\exp[-u_0(r)/kT] = \langle \exp[-u(r\omega_1\omega_2)/kT] \rangle_{\omega_1\omega_2} \quad (5)$$

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  $y(r\omega_1\omega_2) \equiv \exp[u(r\omega_1\omega_2)/kT]g(r\omega_1\omega_2)$ . The fluid structure calculated from the f-expansion is generally better than from the u-expansion, though there are still considerable discrepancies. The thermodynamic properties calculated from the f-expansion are generally more accurate than the u-expansion when the molecules possess nonspherical cores. When the cores are nearly spherical the results from the two theories are similar (ref.4). The f-expansion does not seem to have been applied to mixtures.

Among the most difficult fluids to treat are those in which the molecules have a significantly nonspherical shape together with strong electrostatic forces. The fluid structure is then dependent on both the shape and electrostatic effects, so that there is no simple reference fluid from which to perturb. A prototype model system of this sort is a fluid of hard dumbbells (HD) with embedded point charges (PC) placed in a quadrupolar symmetry; we call this the HD + PCQ model. Computer simulation results for the Helmholtz energy of such a fluid (bond length  $\ell^* = \ell/\sigma = 0.6$ ) are shown in Fig. 6, together with the results of several perturbation theories. The f-expansion (dotted line) overestimates the effect of the electrostatic forces on the free energy. An obvious, but naive, choice of reference fluid is one of hard dumbbells, so that  $A_0 = A_{HD}$  and

$$A = A_{HD} + A_1 + A_2 + \dots \quad (6)$$

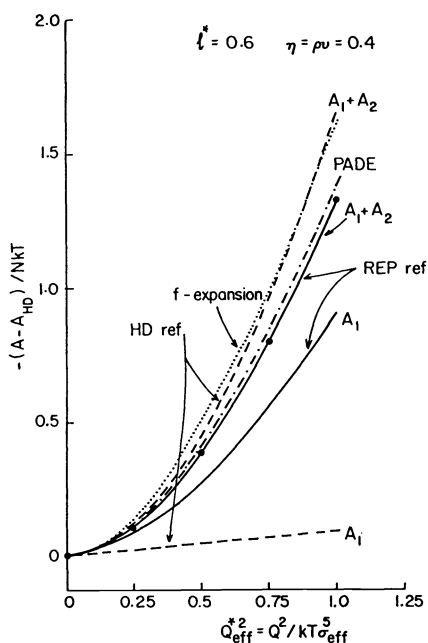


Fig. 6. The electrostatic force contribution to the free energy of the HD + PCQ fluid as a function of quadrupole strength  $Q_{\text{eff}}^{*2}$ , for dumbbells with bond length  $\ell/\sigma = 0.6$  at reduced density  $\rho v = 0.4$ . Here  $\sigma$  is the hard sphere (site) diameter,  $\rho$  is number density,  $v$  is volume of the dumbbell, and  $\sigma_{\text{eff}}$  is the diameter of a sphere having the same volume as the dumbbell. Further details are given in the text. (From Wojcik and Gubbins, ref. 27).

The results for both first and second order treatments (with  $A_1$  and  $A_2$  calculated exactly by computer simulation) are shown as dashed lines in Fig. 6. The first order theory gives results that are much too low, while the second order theory overestimates the electrostatic effects and is no better than the  $f$ -expansion. This hard dumbbell 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. (6) is modified to

$$A = A_{REP} + A_1 + A_2 + \dots \quad (7)$$

where  $A_{REP}$  is the free energy of the repulsive force reference fluid. This series has been recently studied by Wojcik and Gubbins (ref. 27) using Monte Carlo simulations in which the various terms  $A_{REP}$ ,  $A_1$ , and  $A_2$  are evaluated exactly. The results are shown in Fig. 6 as solid lines. 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  $A$ . The structure results for the REP fluid are intermediate between those for the HD and HD + PCQ fluids. While eqn. (7) is clearly superior to (6), it is still not a satisfactory solution to the problem because of the difficulty in calculating  $A_2$  by analytic means.

In view of the poor convergence of the series of eqn. (6), Rasaiah et al. (ref. 28) and Martina et al. (ref. 29) have suggested the Padé approximant,

$$A = A_{HD} + A_1 + A_2/(1 - A_3/A_2) \quad (8)$$

To avoid the difficulty of calculating the HD correlation functions that appear in  $A_2$  and  $A_3$ , these authors suggested replacing the functions by the corresponding functions for an effective hard sphere (HS) fluid. The  $A_2$  and  $A_3$  terms then reduce to the simple forms for molecules with hard sphere cores. Several prescriptions have been suggested for determining the best hard sphere diameter in such a scheme, including equating the residual free energies or compressibility factors for the HD and HS fluids. The dash-dot line in Fig. 6 shows the result of using eqn. (8), with hard sphere diameters determined from the residual free energies. In practice, the  $A_1$  term is often small enough to be neglected. The Padé of eqn. (8) is seen to give quite good results.

Comparisons of the nonspherical reference system perturbation theory with experimental data for mixtures seem to have been limited to nonpolar liquids, using the Kihara model with Boublik's theory (refs. 30-32) or the Lennard-Jones interaction site model (ref. 33).

## MIXTURES WITH STRONG INTERACTIONS (ASSOCIATING MOLECULES)

In fluids with strong, highly directional, attractive forces (e.g. due to hydrogen bonding, charge transfer, etc.) the perturbation theories described in the previous section fail, and can even give physically impossible results (ref. 34,35). In such cases the effects of these strong forces must be incorporated in any theory from the beginning. For example, the strength of the hydrogen bond between two water molecules is about 6 kcal/mole or  $10RT$  at room temperature, where  $R$  is the gas constant and  $T$  the absolute temperature. In this section we first review some of the theoretical approaches to such fluids, and then give some recent results from one of these theories.

### Theories

The chemical theory is the oldest method for treating associating mixtures. It treats the strongly anisotropic attractions as chemical reactions with a corresponding equilibrium constant. The properties of the mixture are then related to this equilibrium constant through thermodynamic identities. For example, for a solvating mixture of molecules  $A$  and  $B$  that 'bond' in a one to one ratio, one assumes that  $A$  and  $B$  are in equilibrium with a dimer  $AB$ . One can then either assume that the three species ( $A$ ,  $B$ , and  $AB$ ) form an ideal mixture or take into account the nonideality through an empirical equation such as van Laar's, thus adding more adjustable parameters. We are then faced with the problem of not only determining the equilibrium constant, but also the temperature dependence of the equilibrium constant and any other physical parameters. This approach is not incorrect; as we will see, classical statistical mechanical theories treat the hydrogen bond and the chemical bond in a similar way, but this treatment requires much experimental data to fit the empirical parameters.

One of the earliest statistical mechanical theories of hydrogen bonding is due to Andersen (refs. 34,35). For the case in which molecules contain only one attractive site, Andersen noted that because a hydrogen bond is short ranged and highly directional, repulsive core interactions would allow dimers but no higher  $s$ -mers to form. To take into account the strength of the hydrogen bond, Andersen wrote a cluster expansion in terms of two densities: the overall density and a density weighted by the strength of the hydrogen bond. Because of the restriction to only dimer formation, Andersen was able to show that many diagrams in the expansion are negligible. This theory was developed for the structure of the hydrogen-bonded fluid, but no calculations of the thermodynamic properties were made. Andersen's influence can be seen in some of the most recent papers on highly directional, attractive interactions (ref. 36).

Chandler and Pratt (ref. 37) developed a theory to describe the intramolecular structure of molecules based on intermolecular and external forces. The theory was developed for non-rigid bonds of chemical strength using a physical cluster expansion. The atom-atom bond was modeled with a spherically symmetric attraction. Cummings and Stell (ref. 38) also used a spherically symmetric bonding potential in their solution of the PY approximation for the chemical equilibrium  $A + B \rightleftharpoons AB$ . Since in both of these theories atoms are bonded to form molecules, any orientational dependence of the bonding potential can be neglected. Since the orientational dependence of the hydrogen bond is one of its most important characteristics, this dependence must be fundamental to any theory describing a hydrogen-bonding fluid. Therefore, we conclude that although the above two theories are capable of describing chemical equilibrium, they cannot, in their present form, be applied to the problem of anisotropic attractions.

Recently, Cummings and Blum (ref. 39) have included the directional character of the interaction in their theoretical study of a model for water. They give the solution in the PY approximation for a pure fluid of hard spheres with tetrahedrally arranged charges. The short range character of the hydrogen bond is modeled by surface adhesion (i.e. an infinitesimally wide and infinitely deep potential well) and the angular dependence of the interactions are approximated by a truncated spherical harmonic expansion.

Wertheim (ref. 36) also treats the problem of molecules interacting with highly directional attractive forces explicitly. Like Andersen, he introduces the geometry of the interaction at an early stage. However, Wertheim shows that graph cancellation due to steric effects is simpler and more effective if one uses a fugacity expansion in terms of two densities: the equilibrium monomer density and the (initial) overall number density. By assuming that only dimers and no higher s-mers form, Wertheim was able to greatly simplify the expansion. The resulting equations are applicable to a pure fluid with short-ranged, highly orientationally dependent attractive forces and hard repulsive cores, such that only dimers form. Wertheim has recently extended his theory to multiple attraction sites per molecule (refs. 40,41).

Chapman *et al.* (ref. 42) have extended Wertheim's theory to binary mixtures of components A and B in which only AB dimers can form (i.e., no AA or BB dimers form). The monomer density and overall density are then related by the following equation:

$$\rho_a = \rho_a^{(1)} + \rho_a^{(2)} \quad (9)$$

where  $\rho_a$  is the overall number density of component  $\alpha$ ,  $\rho_a^{(1)}$  is the density of monomers of component  $\alpha$  at equilibrium (after dimers have formed), and  $\rho_a^{(2)}$  is the density of  $\alpha$  molecules that are present as dimers at equilibrium. The fraction of monomers of component  $\alpha$ ,  $X_\alpha = \rho_a^{(1)}/\rho_a$ , is calculated in terms of  $Q$

$$Q = \int g_R(r_{12}) f_{HB}(12) d(12) \quad (10)$$

where  $g_R(r_{12})$  is the pair distribution function for the reference system,  $f_{HB}(12)$  is a Mayer  $f$  function defined by  $f_{HB}(12) = \exp[-\beta u_{HB}(12)] - 1$ , where  $u_{HB}(12)$  is the hydrogen-bond interaction, and the integration is performed over all possible molecular separations and averaged over all orientations. The resulting expression for the change in configurational Helmholtz free energy is given by

$$\frac{\beta \Delta A}{V} = \sum_\alpha \rho_\alpha \left( \log(X_\alpha) - \frac{X_\alpha}{2} + \frac{1}{2} \right) \quad (11)$$

where  $\Delta A$  is the Helmholtz free energy of the associating mixture minus that of the reference mixture,  $V$  is the volume, and  $\beta$  is  $1/k_B T$  where  $T$  is the temperature and  $k_B$  is Boltzmann's constant.

Chapman *et al.* (refs. 42,43) have solved the above equations for a solvating mixture of components A and B that interact with off-center point charge dipoles of equal magnitude and opposite sign. In their model, the like pairs interact as hard spheres and the unlike pairs interact as hard spheres with a sum of coulombic interactions. They find excellent agreement with computer simulation results when the coulombic interaction is of short enough range so that few higher s-mers form.

### Some results

In this section we give some of the results obtained by Chapman *et al.* (refs. 42,43) for solvating AB mixtures. In Figs. 7-9 we show theoretical calculations of the fraction of monomers of each component and of the excess Gibbs energy and volume of mixing at constant pressure,  $P\sigma^3/k_B T = 0.9925$ , for various values of the reduced dipole moment. In these calculations we have used a coulombic interaction cutoff distance  $r_c$  of  $1.0 \sigma$ . In Fig. 7, the fraction of monomers is the fraction of component A or B that exists as a monomer in solution. In Figs. 8 and 9 are shown the large negative values for the excess properties that are common in strongly solvated mixtures e.g. acetic acid/triethyl amine and acetone/chloroform. These figures show that the theory produces qualitatively expected results for mixtures over a range of strengths of interaction from ideal solution to chemical bonding.

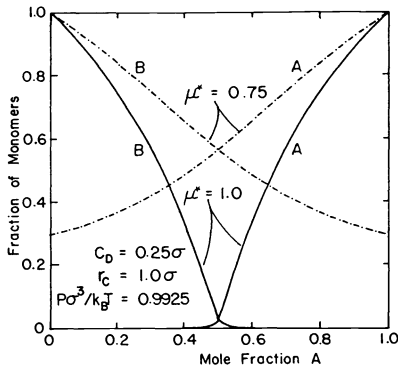


Fig. 7. The fraction of monomers,  $\rho_a^{(1)}/\rho_a$ , of each component as a function of mole fraction A (in a mixture of A and B with AB association) for two values of the reduced dipole moment,  $\mu^* = \mu/(kT\sigma^3)^{1/2}$ . (From Chapman et al., ref. 43.)

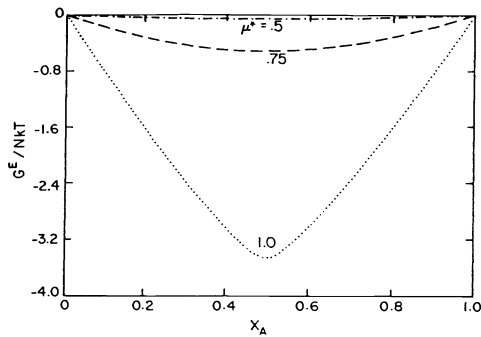


Fig. 8. The excess Gibbs energy, at the same conditions as in Fig. 7. (From Chapman et al., ref. 43.)

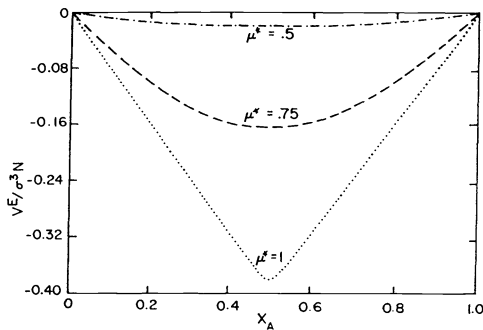


Fig. 9. The excess volume, at the same conditions as in Fig. 8. (From Chapman et al., ref. 43)

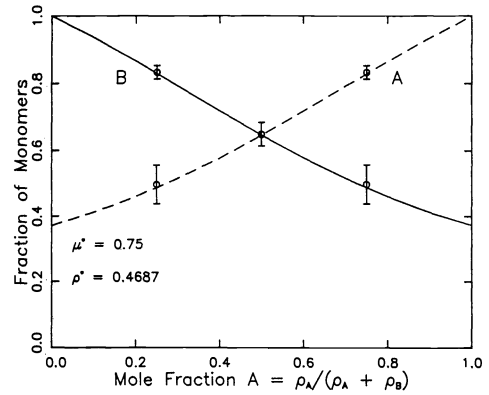


Fig. 10. Comparison between Monte Carlo simulation results (circles) and theory (curves) for the fraction of monomers of each component at  $\mu^* = 0.75$ ,  $\rho^* = 0.4687$ , and  $r_c = 0.55\sigma$ . (From Chapman et al., ref. 42.)

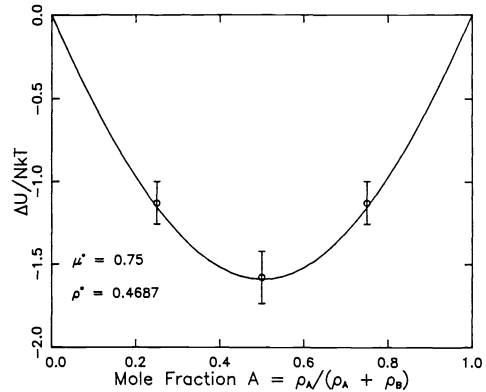


Fig. 11. Comparison between Monte Carlo results (circles) and theory (curves) for the internal energy change on mixing for the same mixture and conditions as in Fig. 12. (From Chapman et al., ref. 42.)

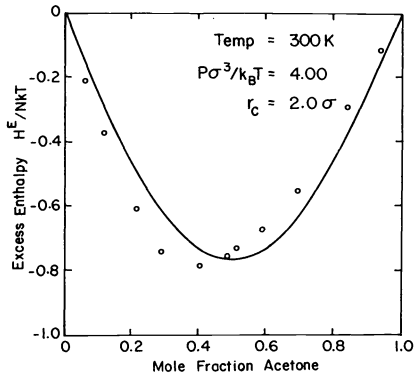


Fig. 12. The excess enthalpy of chloroform - acetone mixtures at 300K from theory (curve) and experiment (points). (From Chapman et al., ref. 43.)

In Figs. 10 and 11 Metropolis Monte Carlo simulation results are compared with theory for the fraction of monomers and change in internal energy on mixing at constant density. The simulation results are for  $\mu^* = \pm 0.75$  and  $\rho^* = 0.4687$  with 108 total particles. The cutoff for the coulombic interaction  $r_c$  was chosen to be  $0.55\sigma$  so that only dimers could form. The averages were taken over  $4.5 \times 10^6$  configurations after equilibration of at least  $2. \times 10^6$  configurations. The error bars, calculated based on averages over  $5. \times 10^5$  configurations, represent one standard deviation from the mean. Similarly good agreement between theory and simulation was found for  $\mu^* = \pm 1.00$  (ref. 42).

The potential models used by Chapman *et al.* are too crude to expect quantitative predictions for real mixtures, but it is of interest to see if the theory predicts qualitatively correct results. Chapman *et al.* (43) have compared the theory with experimental data for the chloroform-acetone mixture at about 300K. The results for the excess enthalpy are shown in Fig. 12. Dipole and quadrupole moments from the literature were used to determine the magnitude and location of the charges (one of the charges was arbitrarily assigned to the center of the sphere for each species), and sphere diameters were determined from Lennard-Jones  $\sigma$  parameters. The reduced pressure  $P\sigma^3/k_B T = 4.0$  corresponds to a pure component reduced density of  $\rho^* = 0.7$ , which is a typical liquid density. Agreement between theory and experiment is good considering the crude model.

## CONCLUSION

There have been major advances in the statistical mechanics of polar liquids in the last fifteen years, and these theories give a good account of model polar fluids, particularly for molecules that are not too nonspherical. As for other types of liquids, a major problem is the need for more realistic and accurate intermolecular potential models to describe real liquids. At present theorists are forced to work with quite crude models, particularly for polar and associating molecules. Some problems also remain in the statistical mechanics of polar fluids. We do not yet have a satisfactory theory for molecules that are both nonspherical in shape and strongly polar. For the case of associating molecules, further theoretical developments are needed in order to deal with molecules with multiple attractive sites and ones that form s-mers with  $s > 2$ .

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