

# The thermodynamic properties of dipolar fluids

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The Thermodynamic Properties of Dipolar Fluids

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To Gail and Sam

### Abstract

The role of intermolecular forces in the phase behaviour of mixtures of polar molecules is investigated using a Statistical Mechanical approach. The quantitative description of such phase behaviour is obtained through a direct application of the thermodynamic properties of the polar mixture which are calculated via the ensemble-average formalism offered by Statistical Mechanics (McQuarrie, 1976). The structural and thermodynamic properties of a fluid composed of molecules interacting via long-ranged nonspherically symmetric forces are far less readily obtained than those interacting via spherically symmetric forces (Barker and Henderson, 1976). The simplest model of such a long-ranged anisotropic potential is the dipole-dipole potential truncated at molecular-sized distances by a purely repulsive hard core interaction. Even for this model potential, the usually successful simulation methods (Monte Carlo and Molecular Dynamics) are not reliable. It has been found using these methods that different boundary conditions for a finite volume sample have given different thermodynamic and structural results (Valleau and Whittington, 1977).

In this thesis, the investigation of the effect of long-ranged interactions on the properties of mixtures of dipolar hard spheres will be based on the solution of the Ornstein-Zernike equation. This exact integral equation is supplemented by the closure rule of the Mean Spherical Approximation. The procedure of decoupling the resulting angular-dependent integral equation is an extension of the methods of Wertheim (1971). Wertheim has solved the single component dipolar fluid problem subject to an assumed form of the angular

dependence for the correlation functions of the Ornstein-Zernike equation. Given this Ansatz, the multi-dimensional Ornstein-Zernike equation can be decomposed to a set of one-dimensional Ornstein-Zernike-like equations. For mixtures of equal-sized molecules, these equations reduce to an effective single component fluid (Adelman and Deutch, 1973). However, the formulation of Adelman and Deutch is not justified for the more interesting case of nonequal diameters.

This thesis shows that the Mean Spherical Approximation can be solved in closed form for dipolar mixtures of nonequal diameters. These closed form expressions provide self-consistent equations for certain fundamental variables  $K_{\alpha\beta}$ .

It can be shown that the structural and bulk properties of a mixture of dipolar hard spheres of different diameters are determined through the solution of a set of self-consistent equations for the parameters,  $K_{\alpha\beta}$  ( $\alpha, \beta = 1, 2$ ). The details of these equations for the  $K_{\alpha\beta}$  are given through an application of the Wiener-Hopf techniques of Baxter (1970). The  $K_{\alpha\beta}$ 's play a central role in the calculation of the thermodynamic properties of the dipolar mixture (Chapter 3). In order to calculate any thermodynamic property, the solution of these equations for the  $K_{\alpha\beta}$ 's must be obtained numerically. The usual numerical root-searching routines (Acton, 1970) fail dismally, and so new techniques were developed to solve the coupled set of equations for the  $K_{\alpha\beta}$ 's (Chapter 3). These numerical solutions for the  $K_{\alpha\beta}$ 's were next manipulated to obtain an excess Gibbs free energy of the dipolar mixture. A study of the curvatures of the excess Gibbs free energies

then allowed the behaviour of the mixing properties of the dipolar mixture to be determined in terms of molecular variables.

It is found that dipolar forces are responsible for the phase separation of the model mixture. The types of such phase behaviour which are predicted by this calculation are very similar to the different categories (Types II, III, III<sub>m</sub>) of the phase behaviour for van der Waals mixtures (van Konynenburg, 1968; Scott and van Konynenburg, 1970).

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I wish to warn the reader before entering Chapter 3 to take to heart the sage words of Acton (1970):

"I have tried to make my explanations clear, but sad experience has shown that you will not really understand what I am talking about until you have made some of the same mistakes that I have made. I hesitate to close a preface with a ringing exhortation for you to go forth to make fruitful mistakes; somehow, it doesn't seem quite the right note to strike! Yet, the truth it contains is real. Guided, often laborious, experience is the best teacher for an art. If all you desire is a conversational knowledge of an art, you've chosen the wrong subject, the wrong author, and just possibly the wrong profession. It is one of the minor paradoxes of our language that, even in the 1970s, you learn how to solve real problems only by getting your hands dirty with rational numbers - although rational problems can frequently be solved only with real numbers. Good luck!".

## Chapter 1

### Statistical Mechanics of Nonspherical Molecules

#### 1. Introduction

The fundamental problem of classical equilibrium statistical mechanics is the calculation of the partition function (McQuarrie, 1976). All of the usual thermodynamic properties are obtainable from the partition function, thus giving it a central role in their calculation from molecular parameters. Considerable progress has been made in these calculations for systems made up of molecules which interact through spherically symmetric pair intermolecular potentials (Andersen, 1975; Barker and Henderson, 1976; Singer 1973). However, the treatment of molecules with nonspherical forces is complicated further by angular dependence.

The well-known phase space integral for the canonical partition function,  $Q(N, V, T)$  is (Hill, 1956)

$$Q(N, V, T) = (N! h^{fN})^{-1} \int \prod_{i=1}^N d\tilde{Q}_i d\tilde{P}_i e^{-\beta H(\tilde{P}_1, \tilde{Q}_1, \dots, \tilde{P}_N, \tilde{Q}_N)}. \quad (1)$$

Here,  $N$  identical linear molecules of mass  $m$  interact within a closed volume  $V$  and at a fixed temperature  $T$ , re-defined in terms of the Boltzmann constant  $k$  as  $\beta = (kT)^{-1}$ ;  $h$  is Planck's constant and  $f$  is the number of degrees of freedom per molecule. The Hamiltonian  $H$  is a function of the set of spatial and orientational coordinates  $\tilde{Q}_i$  of each molecule  $i$  and the set of conjugate momenta  $\tilde{P}_i$ . For a linear molecule  $i$ , these are the centre of mass coordinates  $\vec{r}_i$  and its associated linear momentum  $\vec{P}_{\vec{r}_i}$ , along with the orientational coordinates  $\Theta_i, \phi_i$  and conjugate angular momenta

$P_{\theta_i}$ ,  $P_{\phi_i}$ . The differential element in phase space is the totality of  $dQ_i dP_i$  where symbolically,

$$\begin{aligned} dQ_i &= d\vec{r}_i d\theta_i d\phi_i \\ dP_i &= d\vec{P}_{\vec{r}_i} dP_{\theta_i} dP_{\phi_i} ; \end{aligned} \quad (2)$$

that is

$$\prod_{i=1}^N dQ_i dP_i = \prod_{i=1}^N d\vec{r}_i d\theta_i d\phi_i d\vec{P}_{\vec{r}_i} dP_{\theta_i} dP_{\phi_i}.$$

For a system of rigid linear molecules the Hamiltonian is

$$\begin{aligned} H &= \sum_{j=1}^N \left( \frac{P_{\vec{r}_j}^2}{2m} + \frac{P_{\theta_j}^2}{2I} + \frac{P_{\phi_j}^2}{2I \sin^2 \theta_j} \right) \\ &\quad + U(\vec{r}_1, \theta_1, \phi_1, \dots, \vec{r}_N, \theta_N, \phi_N), \end{aligned} \quad (3)$$

where  $I$  is the moment of inertia about an axis perpendicular to the axis of symmetry in the linear molecule and  $U$  is the total intermolecular potential for the configuration  $\vec{r}_1, \theta_1, \phi_1, \dots$

$\dots, \vec{r}_N, \theta_N, \phi_N$ . The integrations over  $\vec{P}_{\vec{r}_j}$ ,  $P_{\theta_j}$  and  $P_{\phi_j}$  can be performed using standard integral techniques. In particular, the integration over  $P_{\phi_j}$  introduces the factor  $\sin \theta_j$  into the integrand, which provides the angular volume element

$$\sin \theta_j d\theta_j d\phi_j = d\vec{\Omega}_j,$$

where

$$\vec{\Omega}_j \equiv (\theta_j, \phi_j).$$

The final result, given in terms of

$$\begin{aligned} \Lambda_r &= h^2 / (2\pi I k T) \\ \Lambda_t &= h / (2\pi m k T)^{\frac{1}{2}} \end{aligned}$$

and

$$Z(N, V, T) = \int \prod_{j=1}^N d\vec{r}_j d\vec{\Omega}_j e^{-\beta U(\vec{r}_1, \vec{\Omega}_1, \dots, \vec{r}_N, \vec{\Omega}_N)}, \quad (4)$$

is

$$Q(N, V, T) = Z(N, V, T) / (N! \Lambda_r^N \Lambda_t^{3N}), \quad (5)$$

where, for linear molecules without the vibrational degrees of freedom,  $f$  is five. The translational and rotational motions are described in  $\Lambda_t$  and  $\Lambda_r$ , and the intermolecular potential is to be averaged over all configurations and is incorporated in the configurational integral,  $Z(N,V,T)$ . Here, the differentials in  $Z(N,V,T)$  are over the volume elements  $d\vec{r}$  and  $d\vec{\Omega}$  in contrast to the phase space differentials which lack the Jacobian factor  $\sin \Theta$

The calculation of the thermodynamic properties from the partition function follows from the Helmholtz free energy  $A$  given by

$$\begin{aligned} A(N,V,T) &= -KT \ln Q(N,V,T) \\ &= KT \ln (N! \Lambda_r^N \Lambda_t^{3N}) - KT \ln Z(N,V,T). \end{aligned} \quad (6)$$

On the right hand side of equation (6), the first term is merely the contributions of kinetic energies of an ideal gas to the free energy at the same conditions of  $N$ ,  $V$ ,  $T$ . Thus the configurational integral  $Z$  contains all of the effects of molecular interactions on the thermodynamic properties. However, any direct calculation of the configurational integral is prohibitive for dense systems, e.g., liquids. Fortunately an alternative approach is provided by the method of distribution functions (McQuarrie, 1976). Here the calculation of the thermodynamic properties is reformulated as a two part problem. The first stage involves the calculation of the distribution functions themselves. These distribution functions are then utilized in the final stage where the thermodynamic properties are calculated. In this approach, not only are the bulk thermodynamic properties of the system calculated but also the molecular structure of the system is detailed in the distribution functions.

## 2. Molecular Distribution Functions and Liquid Structure

Complete details of liquid structure are given in the N-body distribution of the molecules as dictated by the total potential  $U(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2, \dots, \vec{r}_N, \vec{\Omega}_N)$ . However, such detailed information is unnecessary for those liquids for which it is assumed that the total potential is made up of pair interactions only. There, the pair distribution function is closely associated with a structural quantity which is experimentally measured in the scattering of radiation by liquids and which plays an important role in the calculation of thermodynamic properties.

The probability of finding a molecule spatially at  $\vec{r}_1$  and orientated at  $\vec{\Omega}_1$  within the respective volume increments  $d\vec{r}_1$  and  $d\vec{\Omega}_1$  and another one at  $\vec{r}_2, \vec{\Omega}_2$  within  $d\vec{r}_2$  and  $d\vec{\Omega}_2$  is

$\rho^{(2)}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) d\vec{r}_1 d\vec{\Omega}_1 d\vec{r}_2 d\vec{\Omega}_2$ , where  $\rho^{(2)}$  is the pair distribution function defined by

$$\rho^{(2)}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = \frac{N(N-1)}{Z(N, V, T)} \int \prod_{j=3}^N d\vec{r}_j d\vec{\Omega}_j e^{-\beta U(\vec{r}_1, \vec{\Omega}_1, \dots, \vec{r}_N, \vec{\Omega}_N)}. \quad (7)$$

Any molecular property which is a function of the configuration of pairs of molecules only, can be ensemble averaged over the pair distribution function. If  $X(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  is the molecular pair property, its average value is the ensemble average,  $\bar{X}$ , given by

$$\begin{aligned} \bar{X} = & \iint d\vec{r}_1 d\vec{\Omega}_1 d\vec{r}_2 d\vec{\Omega}_2 X(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) \\ & \times \rho^{(2)}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2). \end{aligned} \quad (8)$$

Before considering such molecular functions which average to the appropriate thermodynamic properties, it is appropriate to define the structural quantity customarily obtained from experimental data. This is the pair correlation function  $g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  and is defined by

$$g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = \rho^{(2)}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) / (\rho^{(1)}(\vec{r}_1, \vec{\Omega}_1) \rho^{(1)}(\vec{r}_2, \vec{\Omega}_2)) \quad (9)$$

where  $\rho^{(1)}(\vec{r}, \vec{\Omega})$  is the one body distribution function at  $\vec{r}$  and  $\vec{\Omega}$ . For isotropic homogeneous systems  $\rho^{(1)}$  is independent of positions and angles and equals the total number density  $\rho$  divided by  $\int d\vec{\Omega}$ . Thus the pair correlation function for a homogeneous, isotropic system is

$$g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = \Omega^{-2} \rho^{(2)}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) / \rho^2$$

where  $\Omega$  is the angular volume  $\int d\vec{\Omega}$ . For spherically symmetric potentials,  $g$  is only a function of the distance of separation between molecules,  $r_{12} = |\vec{r}_2 - \vec{r}_1|$ . Such radial dependence has given  $g$  the more physical name of the radial distribution function.

Equation (9) will be used to define  $g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  even though some authors have defined the radial distribution function as the unweighted angle-averaged  $g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  (Barker and Henderson, 1976). Also  $\Omega^{-1} \rho g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  is the conditional probability density that given a molecule is at  $\vec{r}_1, \vec{\Omega}_1$  another molecule is found at  $\vec{r}_2, \vec{\Omega}_2$ . Thus, the averaged structure of the liquid is measured by the angle-dependent radial distribution function.

In addition, the mechanical thermodynamic properties of a system are given in terms of the radial distribution function if the total potential of any configuration is a sum of terms arising from pairs of interacting molecules. The statement of pairwise additivity of the potential is written as

$$U(\vec{r}_1, \vec{\Omega}_1, \dots, \vec{r}_N, \vec{\Omega}_N) = \sum_{1 \leq i < j \leq N} u(\vec{r}_i, \vec{\Omega}_i, \vec{r}_j, \vec{\Omega}_j) \quad , \quad (10)$$

where  $u(\vec{r}_i, \vec{\Omega}_i, \vec{r}_j, \vec{\Omega}_j)$  is the intermolecular interaction between two molecules located at  $\vec{r}_i, \vec{\Omega}_i$  and  $\vec{r}_j, \vec{\Omega}_j$ . However,  $u$  is a complicated function of these spatial and orientational coordinates. Nevertheless, for a wide class of pair interactions (e.g. electrostatic multipole interactions),  $u$  is dependent only on the relative coordinates. These are the direction and magnitude of the intermolecular axis  $\hat{\vec{r}}_{ij}$  and  $|\vec{r}_j - \vec{r}_i|$  and the orientations of the molecules relative to  $\hat{\vec{r}}_{ij}$ . Here  $\hat{\vec{r}}_{ij} = (\vec{r}_j - \vec{r}_i)/|\vec{r}_j - \vec{r}_i|$  is the unit vector along the  $ij$  intermolecular axis. This dependence of  $u$ , and so  $U$ , on relative coordinates directly implies the distribution functions also have the same dependence. This will be discussed further in the following Chapter.

Expressions for the ensemble averages of the intermolecular pair potential and the associated virial give the internal energy and virial pressure, respectively. Thus, the internal energy  $E$  and virial pressure  $p$  are

$$E = E_{\text{kinetic}} + \frac{\rho^2}{2\Omega^2} \iint d\vec{r}_1 d\vec{\Omega}_1 d\vec{r}_2 d\vec{\Omega}_2 g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) \times u(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) \quad , \quad (11)$$

$$p = \rho kT - \frac{\rho^2}{6V\Omega^2} \iint d\vec{r}_1 d\vec{\Omega}_1 d\vec{r}_2 d\vec{\Omega}_2 g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) \times \vec{r}_{12} \cdot \vec{\nabla} u(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) \quad (12)$$

In the above equation (11),  $E_{\text{kinetic}}$  is the kinetic energy of an ideal gas at the same  $N$  and  $T$  and possessing the same number of degrees of freedom. These formulae are quite general for non-spherical potentials. For linear molecules the normalization factor  $\Omega = 4\pi$  and  $\vec{\Omega}_i = (\theta_i, \phi_i)$ . For nonlinear molecules  $\Omega = 8\pi^2$  and the complete set of Euler angles  $\vec{\Omega}_i = (\theta_i, \phi_i, \psi_i)$  locate the direction of the molecule, and the angular volume integration augmented by  $\int d\psi_i$ . The  $\vec{\nabla}$  operator is defined with respect to the intermolecular axis  $\vec{r}_{12}$ . For spherically symmetric potentials, the angular dependence disappears in the normalization.

It follows that the radial distribution function is of great interest in understanding the molecular liquid structure and calculating thermodynamic bulk properties. However, it is as difficult to calculate directly from its definition as the configurational integral in the original format. This can be seen from the fact that  $g$  is only two molecular averages different from  $Z(N, V, T)$ . The advantages of this reformulation for calculating thermodynamic properties from  $g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  rather than  $Q(N, V, T)$  are not utilized unless  $g$  itself is known. The radial distribution function can be determined from the intermolecular potential as seen in equations (7) and (9). However,  $g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  can alternatively be obtained as the solution to a hierarchy of integral equations which can be derived from its definition. This approach, developed by Kirkwood, Born and Green and others has resulted in different hierarchies of integral equations appropriately named (Hill, 1956). The basic difficulty encountered in these approaches is the decoupling

of the zeroth order equation for the radial distribution function from the higher order integral equations, which requires approximations. Another method is given in the Ornstein-Zernike integral equation, which, by itself, is the definition of another correlation function called the direct correlation function. Just as the integral equations in the hierarchy require certain closure approximations the Ornstein-Zernike equation also requires an approximate closure rule. This closure rule is an equation of a further functional dependence between the direct correlation function and the radial distribution function. The advantage of the Ornstein-Zernike equation is that reasonable approximations are easier to obtain than in the other techniques. The solutions of the Ornstein-Zernike equation subject to the closure rule will be summarized in the next Section for various intermolecular potentials. Also the applicability of the various closure rules will be discussed.

### 3. Modern Integral Equation Approach

#### 3.1 The Ornstein-Zernike Equation

In a liquid, any two molecules are in constant interaction with each other and their neighbouring molecules. The resulting correlative behaviour for a pair of molecules is given in the definition of the pair distribution function, where all possible configurations of  $N-2$  molecules are averaged for a fixed configuration of molecules 1 and 2. In this regard,  $g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  is then a measure of the total correlation between any two molecules.

As molecules approach each other too closely, they are repelled; so that as  $r_{12} \rightarrow 0$ ,  $q(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2) \rightarrow 0$ . On the other end of the scale, at large distances of separation, molecules behave independently and so  $q(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2) \rightarrow 1$  as  $r_{12} \rightarrow \infty$ . Subtracting this asymptotic behaviour from  $q(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2)$  defines the total correlation function  $h(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2)$  :

$$h(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2) = q(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2) - 1. \quad (13)$$

Physically, from the asymptotic properties of  $q(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2)$ ,  $h(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2)$  approaches -1 as  $r_{12} \rightarrow 0$  and oscillates to zero as  $r_{12} \rightarrow \infty$ .

The oscillatory behaviour which arises from spatial correlations between molecules is shown schematically in Figure 1 for a spherically symmetric potential. These correlations between molecules are considered to arise in the Ornstein-Zernike equation from two effects. One effect is that correlations are directly propagated between the two molecules. The second class of correlations is the result of a third molecule transmitting correlative effects between the two molecules being considered. The respective direct and indirect correlations are the first and second terms in the Ornstein-Zernike equation,

$$h(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2) = c(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2) + \int d\vec{r}_3 d\vec{n}_3 \frac{\rho(\vec{r}_3, \vec{n}_3)}{\Omega} \times c(\vec{r}_1, \vec{n}_1, \vec{r}_3, \vec{n}_3) h(\vec{r}_3, \vec{n}_3, \vec{r}_2, \vec{n}_2). \quad (14)$$

Equation (14) defines the direct correlation function

$c(\vec{r}_1, \vec{n}_1, \vec{r}_2, \vec{n}_2)$ . Note that  $\rho(\vec{r}, \vec{n})$  is the number density at  $\vec{r}, \vec{n}$ .

### 3.2 Closure Rules for the Ornstein-Zernike Equation

The Ornstein-Zernike equation is supplemented by a closure rule which is then used along with equations (13) and (14) to solve for the distribution function  $g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$ . In particular, the closure rule takes the form of expressing  $c(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  in terms of the intermolecular potential  $u(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  and often an explicit dependence on  $h(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$ .

As a preliminary to discussing the possible closure rules, it is worthwhile discussing the zero-density limit, for which the exact behaviour of  $c$  and  $g$  is known. The direct correlation function is dependent only on temperature and the intermolecular potential as the density approaches zero. This is given in the zero-density solution of the Ornstein-Zernike equation. In the limit  $\rho \rightarrow 0$ , equation (14) gives

$$\begin{aligned} c(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) &= e^{-\beta u(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)} - 1 \\ &= f(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) \end{aligned} \quad (15)$$

since the limiting behaviour of  $g$  is

$$g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = e^{-\beta u(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)}.$$

Equation (15) gives the low density behaviour of the exact direct correlation function in terms of the Mayer  $f$  function. In this limit, the direct correlation function is of the same range as the potential. This low density behaviour is also found in the Percus-Yevick and Hypernetted Chain closure rules described below. However, the closure rules differ from each other in the approximations used to incorporate the density dependence of the direct correlation function. In particular, the Percus-Yevick

and Hypernetted Chain approximations are given by the following closure rules:

$$C_{PY}(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2) = f(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2) e^{\beta u(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2)} \times g(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2) \quad (16)$$

and

$$C_{HNC}(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2) = g(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2) - 1 - \ln g(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2) - \beta u(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2) \quad (17)$$

These approximations can be derived by using functional analysis techniques (Percus, 1964) or by examining the different cluster integrals in the density expansions of the distribution functions (Stell, 1964). Equations (16) and (17) reduce to the Mayer function in the low density limit, as given in equation (15). It turns out that the resulting self-consistent integral equation for  $c$  or  $g$  is rarely solvable in closed form. However, the simplicity of the hard sphere potential allows such a treatment, at least in the Percus-Yevick approximation (Thiele, 1963; Wertheim, 1963; Baxter, 1968). All other nontrivial realistic potentials in the Percus-Yevick and Hypernetted Chain approximations have thus far required numerical solutions on high speed computers (Watts, 1973).

Andersen (1975) has recently presented an excellent review on the relative merits of the closure relations in the determination of liquid structure. As a general rule, short-ranged forces in fluids are best described in the Percus-Yevick theory whilst long-ranged attractive forces are more accurately described in the Hypernetted Chain theory. Earlier analyses of cluster integrals of the two theories support this idea. As mentioned previously most of the literature cited is numerical in its presentation as

tables, graphs etc. Usually analytic treatments are precluded by the presence of the radial distribution function in equations (16) and (17). Even the exact and simple zero-density closure rule is nonlinear in the pair potential, probably prohibiting any analytic treatment.

However, further linearization of the low density behaviour of  $C(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  does permit analytic solutions for a special set of pair potentials. The resulting linear closure relation may be used at any density and is known as the Mean Spherical Approximation. It is defined for fluids whose molecules can be described as interacting via a hard sphere repulsive core,  $u_{HS}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$ , adjoining a long-range tail,  $v(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$ . Explicitly,

$$u(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = u_{HS}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) + v(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2), \quad (18)$$

where

$$\begin{aligned} u_{HS}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) &= \infty && \text{if } r_{12} < R \\ &= 0 && \text{if } r_{12} > R, \end{aligned} \quad (19)$$

$R$  being the hard sphere diameter associated with the molecular species. A statement of the closure rule in the Mean Spherical Approximation is then a composite of

$$g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = 0 \quad \text{where } r_{12} < R \quad (20a)$$

and

$$C(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = -\beta v(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) \quad \text{where } r_{12} > R. \quad (20b)$$

It should be noted that equation (20a) is exact and reflects the impenetrability of the hard core. All approximations of the Mean Spherical Approximation are in equation (20b). As  $r_{12} \rightarrow \infty$ , equation (20b) gives the proper asymptotic behaviour of the direct correlation function.

Regardless of the inherent difficulties of justification of the Mean Spherical Approximation in the low temperature-high density regime, it is possible in a number of cases to solve the Ornstein-Zernike equation under its closure rule, and this accounts for its popularity. In summary, the Percus-Yevick and Hypernetted Chain closure rules to the Ornstein-Zernike equations are exact in the zero-density limit but approximate elsewhere and only the Percus-Yevick hard sphere solutions have been obtained analytically. The Mean Spherical Approximation is not even exact at zero density, but a wide variety of analytical solutions are obtainable.

#### 4. The Mean Spherical Approximation

The original motivation of the Mean Spherical Approximation was in lattice statistics. Phase transitions in spin lattice problems are associated with singularities in the partition function. However, it has been shown over the years that although the partition function could not be evaluated for a set of Ising spins, it was possible to calculate the partition function of a thermodynamically equivalent model. Here, the dichotomic spin variables of the Ising model were treated as continuous variables subject to certain constraints. These constraints included the spherical model (Berlin

and Kac, 1952) and the still weaker constraint of the mean spherical model (Lewis and Wannier, 1952). These simpler reformulations showed an easy path to the calculation of the partition function in the thermodynamic limit. The Ising model was then immediately equivalent to a lattice gas of structureless points, subject to these approximate treatments. Within the mean spherical model it is possible to include hard core repulsive forces at each lattice site (Lebowitz and Percus, 1966). As the lattice spacing approaches zero, the system approaches a fluid whose particles interact via a hard core repulsive term plus a long-range tail. The mean spherical constraint is equivalent to a constraint on the direct correlation function of the continuum fluid, equation (20b). The Mean Spherical Approximation is then obtained since equation (20a) is guaranteed from the hard core repulsive forces.

In the early 1970's, a number of publications gave analytic solutions of the Ornstein-Zernike equation for long-range forces in the Mean Spherical Approximation. Most were concerned with potentials of the form  $r^{-\eta}$ , e.g.  $\eta=1$  (the charge-charge potential) or  $\eta=3$  (the dipole-dipole potential). It is more appropriate to review the Mean Spherical Approximation solutions as functions of the potential rather than chronologically. Like the mean spherical model of lattice systems, the Mean Spherical Approximation is indeed an approximation for a physically meaningful model system. From equations (18) and (19), the general class of systems that can be studied by the Mean Spherical Approximation are those fluids whose particle potentials are well represented as hard spheres plus a superimposed attractive tail.

It happens that for electrostatic multipolar interactions these solutions can be obtained analytically (Wertheim, 1971; Blum and Torruella 1972; Blum 1972, 1973).

For example, Wertheim (1971) presented a beautiful application of mathematical methods in his solution of the Mean Spherical Approximation for a single component dipolar fluid. The techniques developed by Wertheim can be generalized to arbitrarily shaped molecules (Blum 1972, 1973; MacInnes and Farquhar 1975). In particular the invariant expansion of correlation functions can be formulated according to the symmetry conditions imposed by the bulk fluid as a whole and the symmetries of the individual molecules (Blum and Torruella, 1972). Blum (1972, 1973) has written a series of papers utilizing these invariant expansions dealing with the transformed Ornstein-Zernike equation and its solution for general multipolar interactions given in the Mean Spherical Approximation.

## 5. Dipolar Mixtures in the Mean Spherical Approximation

These single component results can be extended to multi-component systems with the restriction that all components have the same diameter (Adelman and Deutch, 1973). Thus it is possible to reduce a simple dipolar mixture (differing only in dipole moments) to an effective single component dipolar fluid, as far as its structure and thermodynamic properties are concerned (Sutherland et al, 1974). This was a fortuitous result arising from the indistinguishability of direct correlation functions appropriate for mixtures of hard spheres of the same size but distinguished by, say, different colours. Explicit reference to this reduction will

be given in the next Chapter.

The next step in the logical progression of these theories is to solve the Ornstein-Zernike equation in the Mean Spherical Approximation for general dipolar mixtures of arbitrary diameters and dipole moments. The purpose of this thesis is to obtain their solutions analytically and numerically, and to assess the respective roles played by the attractive and repulsive interactions for liquid-liquid phase transitions in dipolar mixtures.

## 6. Brief Review of Some Previous Work on the Mean Spherical Approximation

For completeness, a review of the long-ranged forces that have been treated by the Mean Spherical Approximation will now be given. Waisman and Lebowitz (1970, 1972a, b) first applied the Mean Spherical Approximation to mixtures of charged hard spheres (primitive model for the electrolytes) for the special case of equal charges and equal sizes. Blum (1975) has extended their results for asymmetric electrolytes of different radii. A similar model for plasmas of charged hard spheres in an electron gas neutralizing background was presented by Palmer and Weeks (1973).

An exponential damping factor can be incorporated into the Coulomb type potential which gives rise to the Yukawa potential. This class of interaction was solved in Mean Spherical Approximation by Waisman (1973a). His result was particularly interesting for here the direct correlation function could be thought of as fitting the

exact behaviour outside a hard sphere as given by computer experiments. The model then provided sufficient information to calculate analytically reasonable values of the radial distribution function for hard spheres. The success of the approach of using the Mean Spherical Approximation to give  $c$  outside the hard core has motivated the Generalized Mean Spherical Approximation (Høye et al., 1974). Here a two parameter function of Yukawa form is added onto the Mean Spherical Approximation for  $c$  outside  $R$ . These parameters,  $K$  and  $Z$ , are adjusted to give consistent thermodynamic calculations for the pressure as given from its various thermodynamic paths. Explicitly, the Generalized Mean Spherical Approximation is

$$h(r_{12}) = -1 \quad \text{for } r_{12} < R$$

and

$$c(r_{12}) = -\beta v(r_{12}) + \frac{K e^{-Z(r_{12}-R)}}{r_{12}} \quad \text{for } r_{12} > R.$$

Its application to the primitive model of electrolytes is a significant improvement over the Mean Spherical Approximation (Stell and Sun, 1975). The radial distribution functions near  $r \gtrsim R$  agree with the Monte Carlo results under this improved approximation for  $c(r)$  in the  $r > R$  region.

The corresponding numerical application to dipolar hard sphere fluids has not been done. However, similar improvement in the radial distribution function just outside the hard core region should be expected. This is a result of the Yukawa form being used for the "outside- $R$ " behaviour of the radial coefficients, rather than these functions being zero as in the Mean Spherical Approximation.

It should be mentioned here that all these functional approximations, including the interpretation as representing the intermolecular potential, have a common property. Each contribution, denoted by  $F(r)$ , to the "outside- $R$ " dependence of  $c(r)$  satisfies the Helmholtz equation,  $\nabla^2 F(\vec{r}, \vec{r}_L) = \alpha^2 F(\vec{r}, \vec{r}_L)$ . The solution of this equation by Fourier analysis has allowed Høye and Stell (1976) to systematically approximate the actual poles of  $\tilde{c}(k)$  in Fourier space. This involves a self-consistent determination of the parameters appearing in  $\tilde{F}(k)$ , the Fourier transform of  $F(r)$ . Indeed, the Mean Spherical Approximation can be systematically extended using Stell's pole approximation technique. The first member in such a hierarchy is the Generalized Mean Spherical Approximation. However, no numerical studies have been published for a dipolar fluid.

Up to this point, all the potentials discussed have been angular independent. The simplest case of a nonspherical interaction is given in the charge-dipole term arising from a multipolar expansion of the electrostatic potential. This case has received much attention by several groups since it would offer a molecular model of solvent effects on electrolytic structure. Adelman and Deutch (1974) and Blum (1974a, b) have independently solved this model for the equal radii case. Blum (1972, 1973) has, in fact, given the formalism for the general multipole-multipole interaction within the Mean Spherical Approximation. Numerical solutions in the Mean Spherical Approximation have been given for oscillatory interactions found in liquid metals (Blum and Narten,

1972) and the short-ranged square well potential (Tago and Swamy, 1973). A hybrid closure rule has been used by Narten, Blum and Fowler (1974) to calculate the structure of a Lennard-Jones fluid at high densities. Excellent results are obtained for the structure. However these must be viewed cautiously since the radial distribution function is also taken as a function of choice of diameter size.

## 7. Some Deficiencies of the Mean Spherical Approximation

The pleasing features of using the Mean Spherical Approximation for long-range interactions are its analyticity and minimization of computer calculations to get thermodynamic and structural properties. However, there are several disturbing features which must be acknowledged. The most important is the low density behaviour of correlation functions given by the Mean Spherical Approximation. The total correlation  $h \rightarrow -u/KT$  as  $\rho \rightarrow 0$  and so it does not agree with the correct limit given in equation (15), viz, the Mayer f-function. It has also been pointed out by Andersen (1975) that this low density behaviour could lead to physically undesirable negative values for the radial distribution function if  $u(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)/KT$  is greater than unity. The second virial coefficient in the Mean Spherical Approximation is also found to be deficient when compared to Keesom's (1912) expressions. On the basis of a similar approximation Andersen (1975) suggested that for low temperatures the Mean Spherical Approximation would underestimate the effect of attractive interactions. In spite of these deficiencies, there is at the moment no other non-perturbative approach to calculate the structure and bulk properties of mixtures dominated by a long-range potential such as

that of the dipole-dipole interaction.

### 8. Exact Statement of the Mean Spherical Approximation for Mixtures

The following Ornstein-Zernike equation is the generalization of equation (15) to mixtures,

$$h_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = c_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) + \sum_{\gamma} \iint d\vec{r}_3 d\vec{\Omega}_3 \frac{\rho_{\gamma}(\vec{r}_3, \vec{\Omega}_3)}{\Omega} \\ \times h_{\alpha\gamma}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_3, \vec{\Omega}_3) c_{\gamma\beta}(\vec{r}_3, \vec{\Omega}_3, \vec{r}_2, \vec{\Omega}_2). \quad (21)$$

This again is the defining relation for direct correlation function

$C_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  between a molecule of species  $\alpha$  and  $\beta$  located at  $\vec{r}_1, \vec{\Omega}_1$  and  $\vec{r}_2, \vec{\Omega}_2$ , respectively. The closure relations can be written down in terms of the distance of the closest approach for hard spheres, i.e.,  $R_{\alpha\beta} = (R_{\alpha} + R_{\beta})/2$ . This assumption of additive diameters is necessary for the solution of closely related hard sphere-like equations to be presented in the next Chapter. In the Mean Spherical Approximation,

$$h_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = -1 \quad \text{if } r < R_{\alpha\beta}, \quad (22a)$$

$$C_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = -\psi_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) / kT \quad \text{if } r > R_{\alpha\beta}. \quad (22b)$$

The central problem is the solution of equations (21) and (22)

for the quantities  $h_{\alpha\beta}$  and  $c_{\alpha\beta}$  as a function of density and temperature. Using the distribution function

$$g_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = h_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) + 1, \quad (23)$$

it is possible to obtain the thermodynamic properties of the fluid mixture from the averages over  $g_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$ . In particular, the internal energy and pressure are written as

$$E = E_{\text{kinetic}} + \frac{1}{2\Omega^2} \sum_{\alpha, \beta} \rho_{\alpha} \rho_{\beta} \int d\vec{r}_1 d\vec{\Omega}_1 d\vec{r}_2 d\vec{\Omega}_2 \times \\ \times u_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) g_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2). \quad (24)$$

$$p = kT \sum_{\alpha} \rho_{\alpha} - \frac{1}{6V\Omega^2} \sum_{\alpha, \beta} \rho_{\alpha} \rho_{\beta} \int d\vec{r}_1 d\vec{\Omega}_1 d\vec{r}_2 d\vec{\Omega}_2 \times \\ \times r_{12} \cdot \nabla u_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) g_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2). \quad (25)$$

Here  $N = \sum_{\alpha} N_{\alpha}$ ,  $N_{\alpha}$  being the number of molecules of species  $\alpha$ ,  $\rho_{\alpha} = N_{\alpha}/V$  the corresponding number density. For dipolar systems finite volume corrections to the indirect correlation function give a non-vanishing contribution to the calculation of the dielectric constant (Wertheim, 1971). However the thermodynamic limit ensures that these finite volume corrections give no contribution to the thermodynamical properties of a dipolar system. For details see Appendix 1.

The solution of the Ornstein-Zernike in the Mean Spherical Approximation equation for this system of dipolar hard spheres will be given in the next Chapter and then an application will be presented for the use of the appropriate thermodynamic functions in liquid-liquid immiscibility.

## Chapter 2

### Correlation Functions for Polar Fluids

#### Method of Solution

##### 1. Introduction

In this Chapter the Ornstein-Zernike integral equation will be solved for a fluid mixture characterized by long-ranged non-central forces. It will be shown that the Mean Spherical Approximation gives closed form expressions for the pair distribution function and the direct correlation function. Both functions contain a spherically symmetric part arising from the short-ranged repulsive forces and a sum of angular terms from the anisotropic attractive forces.

The method of solution is based on operational techniques of Wertheim (1971) which decouple the Ornstein-Zernike equation in "r-space". The equations to be solved are equations (21) and (22) of Chapter 1 subject to the constraints of equations (16) and (17) of the present Chapter. An attempt is made to reconcile the invariant expansion technique of Blum (1972, 1973) and the finite expansion method of Wertheim (1971). The details are to be found in Section 3. The actual process of solution of the final equations (see Sections 3.4, 5 and 6) involves combining the operational techniques of Wertheim (1971) and the factorization methods devised by Baxter (1970) to cope with direct correlation functions of finite range. Some interesting motivational aspects of Wertheim's operational methods are described in the Appendices.

From the solutions, it is found that, as in the single component solution, certain parameters measuring long-ranged correlations between molecules of different species must be determined self-consistently. Such parameters not only give information on liquid structure but also are essential to the calculation of thermodynamic functions. Several limiting cases will be examined (Section 6): the low density result and the special case of equal-sized molecules.

## 2. Pairwise Invariant Functions

### 2.1 Introduction

It is well known that the Ornstein-Zernike equation can be solved for the hard sphere potential in the Percus-Yevick approximation. Wertheim (1963) and Thiele (1963) independently derived the polynomial form for the direct correlation function using Laplace transforms. Their solution also gave the Laplace transform of the indirect correlation function in closed form. Later, corresponding solutions were presented by Lebowitz (1964) for mixtures of hard spheres of different radii within the same approximation. From the convexity of the Gibbs free energy of mixing, Lebowitz and Rowlinson (1964) have shown these mixtures show no immiscibility for all diameter ratios considered. Although this is conditional on the use of the Percus-Yevick approximation, it is strongly reinforced by the molecular dynamics data of Alder (1964). These findings show that differences in repulsive forces alone are not the prime cause of phase transitions in these systems.

A natural extension of hard sphere mixtures is the addition of a long-range weak tail to the hard core repulsion. Such potentials can be treated by the Mean Spherical Approximation as presented in the last Chapter. In particular, for the dipole-dipole interaction, it will be shown that a solution of the Ornstein-Zernike equation in the Mean Spherical Approximation can be obtained analytically.

## 2.2 Choice of Coordinate System

Consider a fluid composed of a mixture of hard spheres of diameter  $R_\alpha$  and containing a nonpolarizable point dipole  $\vec{m}_\alpha$  at the sphere's centre. The configuration of these dipolar hard spheres is easily explained as a special case of that of nonlinear rigid molecules. Consider any Cartesian coordinate system  $i$  fixed in molecule  $i$  and rotating with it. The configuration of molecule  $i$ , with respect to a standard coordinate system  $S$ , is given by locating the origin and orientation of the Cartesian coordinate system  $i$ , relative to the Cartesian coordinate system  $S$ . The displacement vector  $\vec{r}_i$  and the set of Euler angles for the rotation of the coordinate system  $S$  onto  $i$ ,  $i \leftarrow S$ , are symbolized by  $\vec{X}_i$  (Jepsen and Friedman, 1963). Thus, the configuration of any nonlinear molecule is detailed in the six component vector

$$\vec{X}_i = (\vec{r}_i, i \leftarrow S).$$

For nonlinear molecules, the rotation  $i \leftarrow S$  has three components: the  $(\alpha_i, \beta_i, \gamma_i)$  rotation angles. Only two angles  $\alpha_i, \beta_i$  are needed for molecules containing a symmetry axis. Such

linear molecules are independent of the  $\gamma_i$  angle when the Cartesian coordinate system  $i$  is fixed in the centre of the molecule and then rotated so that its  $z$  axis is parallel to the axis of symmetry.

Furthermore,  $\alpha_i$  and  $\beta_i$  are the azimuthal and polar angles,  $\phi_i$  and  $\theta_i$ , respectively. These angles are the orientations of a dipole in dipolar hard spheres if the same argument is applied to the dipole moment vector  $\vec{m}_i(\vec{\Omega}_i)$  is the unit vector  $\vec{s}_i(\vec{\Omega}_i)$ , where for dipolar symmetry, referenced to the standard Cartesian coordinate system  $S$ ,  $\vec{\Omega}_i$  is defined by

$$\begin{aligned}\vec{\Omega}_i &\equiv i \leftarrow S \\ &= (\theta_i, \phi_i)\end{aligned}$$

and  $\vec{s}_i(\vec{\Omega}_i)$  is then given by

$$\vec{s}_i(\vec{\Omega}_i) = (\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i) .$$

In summary, the configuration of a dipolar hard sphere  $i$  is given by

$$\vec{\chi}_i = (\vec{r}_i, \vec{\Omega}_i)$$

where  $\vec{r}_i$  gives the spatial coordinates of the centre of the  $i^{\text{th}}$  sphere and  $\vec{\Omega}_i = (\theta_i, \phi_i)$  gives the orientational coordinates of the dipole's direction. Using these coordinates, the potential is a sum of the short-ranged hard core part plus a dipole-dipole angular part, and can be written in terms of the dipole interaction tensor,

$$\hat{T}(\vec{r}_{12}) = 3(\vec{r}_1 - \vec{r}_2)(\vec{r}_1 - \vec{r}_2) / |\vec{r}_1 - \vec{r}_2|^3 - \hat{U} , \quad (1)$$

as

$$V_{\alpha\beta}(\vec{X}_1, \vec{X}_2) = \infty \quad \text{for } |\vec{r}_{12}| < R_{\alpha\beta}$$

$$= - \frac{\vec{m}_\alpha(\vec{\Omega}_\alpha) \cdot \underline{\underline{I}}(\hat{\vec{r}}_{12}) \cdot \vec{m}_\beta(\vec{\Omega}_\beta)}{|\vec{r}_{12}|^3} \quad \text{for } |\vec{r}_{12}| > R_{\alpha\beta} \quad (2)$$

Here  $\underline{\underline{I}}$  is the unit dyadic (unit tensor in 3 x 3 space), and

$$\vec{r}_{12} = \vec{r}_2 - \vec{r}_1, \text{ and } \hat{\vec{r}}_{12} = \vec{r}_{12} / |\vec{r}_{12}|. \text{ Also } R_{\alpha\beta} = (R_\alpha + R_\beta) / 2.$$

Using  $\vec{m}_\alpha(\vec{\Omega}_\alpha) = |\vec{m}_\alpha| \vec{S}_\alpha(\vec{\Omega}_\alpha)$  we have

$$V_{\alpha\beta}(\vec{X}_1, \vec{X}_2) = \infty \quad \text{for } |\vec{r}_{12}| < R_{\alpha\beta} \quad (3)$$

$$= - \frac{m_\alpha m_\beta}{|\vec{r}_{12}|^3} D(\vec{\Omega}_1, \vec{\Omega}_2, \hat{\vec{r}}_{12}) \quad \text{for } |\vec{r}_{12}| > R_{\alpha\beta}.$$

The angular part of the potential is then

$$D(\vec{\Omega}_1, \vec{\Omega}_2, \hat{\vec{r}}_{12}) = \vec{S}_1(\vec{\Omega}_1) \cdot \underline{\underline{I}}(\hat{\vec{r}}_{12}) \cdot \vec{S}_2(\vec{\Omega}_2).$$

### 2.3 The Role of Rotational Invariants in the Expansion of a Pairwise Invariant Function

The intermolecular potential is unchanged if a pair of molecules is translated or rotated keeping the relative coordinates fixed. There are many other functions in isotropic fluids, e.g., the pair distribution function  $g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$ , which are also invariant to translations and rotations of a pair of molecules, one and two. Such functions are called pairwise invariant functions (Jepsen and Friedman, 1963). Any expansion of these pairwise invariant functions in terms of a complete set of angular basis functions is considerably simplified using the invariance properties. Such a simplification in the original expansion of a pairwise invariant function  $f$  will now be given explicitly (Jepsen and Friedman, 1963).

Classical mechanics gives the equivalence of the translational and rotational operations carried out on rigid bodies and those on the standard coordinate system  $S$ , itself (Goldstein, 1964). Thus the invariance properties of  $f$  can be given in terms of  $f$  being unchanged under arbitrary translations and rotations of the standard Cartesian coordinate system  $S$ . Referenced to the standard Cartesian coordinate system  $S$ ,  $f$  is a function of  $|\vec{r}_1 - \vec{r}_2|$  (from translational invariance of the origin of the  $S$  frame), and, in general, the rotations given in locating each Cartesian coordinate system for molecule 1, molecule 2 and the  $\vec{r}_{12}$  axis. These are symbolized as  $1 \leftarrow S$ ,  $2 \leftarrow S$ , and  $\vec{r}_{12} \leftarrow S$ . Here  $j \leftarrow S$  is a set of the Euler angles  $\alpha, \beta, \gamma$  defined in that rotation of the  $S$  Cartesian coordinate system onto the  $j$  Cartesian coordinate system. The basis set for such angle-dependent functions is the set of Wigner generalized spherical harmonic functions  $D_{mn}^1(j \leftarrow S)$  (Edmonds, 1974) for each rotation  $j \leftarrow S$ . The indices  $m, n, l$  refer to the component angles  $\gamma, \alpha$  and  $\beta$  making up the rotation  $j \leftarrow S$ . Now  $f$  is expanded in terms of these  $D_{mn}^1(j \leftarrow S)$  which are a complete orthogonal set for a given rotation  $j \leftarrow S$ . Then,

$$f = \sum_{\substack{l_1 l_2 l \\ m_1 m_2 \\ n_1 n_2 n}} f_{m_1 m_2 n_1 n_2 n}^{l_1 l_2 l}(\vec{r}_{12}) D_{m_1 n_1}^{l_1}(1 \leftarrow S) D_{m_2 n_2}^{l_2}(2 \leftarrow S) D_{0 n}^l(\vec{r}_{12} \leftarrow S).$$

This already utilizes the property of invariance of  $f$  under translation of the  $S$  coordinate system. Only the relative displacement vector  $\vec{r}_{12}$  occurs rather than  $\vec{r}_1$  and  $\vec{r}_2$  separately. Furthermore,  $f$  is independent of the  $\gamma$  angle in  $\vec{r}_{12} \leftarrow S$ , and so  $m = 0$  appears in the last term. Consider an arbitrary rotation of the  $S$  Cartesian system into a new system  $T$ , i.e.,  $T \leftarrow S$ . From the rotational invariance of  $f$  and the use of

$$D_{mn}^{\ell}(j \leftarrow S) = \sum_{|S| \leq \ell} D_{mS}^{\ell}(j \leftarrow T) D_{Sn}^{\ell}(T \leftarrow S)$$

for  $j = 1, 2, \vec{r}_{12}$ , it follows

$$\begin{aligned} f &= \sum_{\substack{\ell_1 \ell_2 \ell \\ m_1 m_2 n_1 n_2 n \\ s_1 s_2 s}} f_{m_1 m_2 n_1 n_2 n}^{\ell_1 \ell_2 \ell}(\vec{r}_{12}) D_{m_1 s_1}^{\ell_1}(1 \leftarrow T) D_{m_2 s_2}^{\ell_2}(2 \leftarrow T) \\ &\quad \times D_{0s}^{\ell}(\vec{r}_{12} \leftarrow T) D_{s_1 n_1}^{\ell_1}(T \leftarrow S) \\ &\quad \times D_{s_2 n_2}^{\ell_2}(T \leftarrow S) D_{sn}^{\ell}(T \leftarrow S). \end{aligned}$$

The  $T \leftarrow S$  dependence can be simplified from a product of three  $D$  functions to one  $D(T \leftarrow S)$ , and so

$$\begin{aligned} f &= \sum_{\substack{\ell_1 \ell_2 \ell \\ m_1 m_2 n_1 n_2 n \\ s_1 s_2 s}} f_{m_1 m_2 n_1 n_2 n}^{\ell_1 \ell_2 \ell}(\vec{r}_{12}) D_{m_1 s_1}^{\ell_1}(1 \leftarrow T) D_{m_2 s_2}^{\ell_2}(2 \leftarrow T) \\ &\quad \times D_{0s}^{\ell}(\vec{r}_{12} \leftarrow T) \\ &\quad \times \sum_{LM} (2L+1)(2M+1) g_{s_1 s_2 n_1 n_2 sn}^{\ell_1 \ell_2 LM \ell} \\ &\quad \times D_{-(s+s_1+s_2), -(n+n_1+n_2)}^M(T \leftarrow S). \end{aligned}$$

Here  $g$  is a product of four Wigner 3 -  $j$  coefficients

$$\begin{aligned} g_{s_1 s_2 n_1 n_2 sn}^{\ell_1 \ell_2 LM \ell} &= (-)^{s_3+n_3+s_4+n_4} \begin{pmatrix} \ell_1 & \ell_2 & L \\ s_1 & s_2 & s_3 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & L \\ n_1 & n_2 & n_3 \end{pmatrix} \\ &\quad \times \begin{pmatrix} L & \ell & M \\ -s_3 & s & s_4 \end{pmatrix} \begin{pmatrix} L & \ell & M \\ -n_3 & n & n_4 \end{pmatrix}. \end{aligned}$$

Since  $f$  is independent of the  $T \leftarrow S$  rotation, it can be shown

after straightforward algebra that

$$f = \sum_{\substack{l_1 l_2 l \\ m_1 m_2 \\ S_1 S_2}} f_{m_1 m_2}^{l_1 l_2 l} (|\vec{r}_{12}|) (-)^{S_1} \begin{pmatrix} l_1 & l_2 & l \\ -S_1 & S_2 & S_1 - S_2 \end{pmatrix} \\ \times D_{m_1 S_1}^{* l_1} (1 \leftarrow T) D_{m_2 S_2}^{l_2} (2 \leftarrow T) D_{0 S_1 - S_2}^l (\vec{r}_{12} \leftarrow T) \quad (4)$$

where

$$f_{m_1 m_2}^{l_1 l_2 l} = \sum_{n_1 n_2} f_{m_1 m_2 n_1 n_2 n}^{l_1 l_2 l} (|\vec{r}_{12}|) (-)^{m_1} \begin{pmatrix} l_1 & l_2 & l \\ n_1 & n_2 & n \end{pmatrix}.$$

For many years it was thought expedient to use the standard reference frame as that whose  $z$  axis was parallel to the intermolecular axis  $\vec{r}_{12}$ . Then, choosing the  $T$  coordinate system as  $\vec{r}_{12}$  and using

$$D_{mn}^l (\vec{r}_{12} \leftarrow \vec{r}_{12}) = \delta_{mn},$$

it follows that  $f$  is a function of six coordinates only, as given in

$$f = \sum_{\substack{l_1 l_2 l \\ m_1 m_2 S}} f_{m_1 m_2}^{l_1 l_2 l} (|\vec{r}_{12}|) (-)^S \begin{pmatrix} l_1 & l_2 & l \\ -S & S & 0 \end{pmatrix} \\ \times D_{m_1 S}^{* l_1} (1 \leftarrow \vec{r}_{12}) D_{m_2 S}^{l_2} (2 \leftarrow \vec{r}_{12}).$$

These are  $|\vec{r}_{12}|$ ,  $\alpha(1 \leftarrow \vec{r}_{12}) - \alpha(2 \leftarrow \vec{r}_{12})$ ,  $\beta(1 \leftarrow \vec{r}_{12})$ ,  $\beta(2 \leftarrow \vec{r}_{12})$ ,  $\gamma(1 \leftarrow \vec{r}_{12})$  and  $\gamma(2 \leftarrow \vec{r}_{12})$ . The difference in the  $\alpha(j \leftarrow \vec{r}_{12})$  angles occurs as a result of the corresponding  $n$  index for both rotations being the same. However, the final reduction in the number of

independent variables from twelve to six is a great disadvantage.

In particular, if functions simplified by this reduction are used in the Ornstein-Zernike equation, they will give rise to convolution terms which are less tractable than if the functions had been left in the original expansion using the  $\vec{r}_{12}$  dependence as given in the S frame of reference. The complexity introduced into the Ornstein-Zernike equation by using the aforementioned reduction is made manifest in the work done by Steele (1963). Therefore to eschew these complexities, the pair distribution functions in this thesis will be expanded in the set of angular functions  $D_{mn}^1(j \leftarrow S)$ , referenced to the same Cartesian coordinate system S. The conditions imposed by the translational and rotational symmetry of the fluid simplify the expansion as already shown above in equation (4).

Blum and Torruella (1972) have emphasized the rotational invariance of such an expansion as given in the foregoing by defining the basis set of "rotational invariants",  $\phi_{m_1 m_2}^{l_1 l_2 l}(1 \leftarrow T, 2 \leftarrow T, \vec{r}_{12} \leftarrow T)$  as:

$$\begin{aligned} \phi_{m_1 m_2}^{l_1 l_2 l} &= \sum_{S_1 S_2} (-)^{S_1} \begin{pmatrix} l_1 & l_2 & l \\ -S_1 & S_2 & S_1 - S_2 \end{pmatrix} D_{m_1 S_1}^{* l_1}(1 \leftarrow T) \\ &\quad \times D_{m_2 S_2}^{l_2}(2 \leftarrow T) D_{0 \ S_1 - S_2}^l(\vec{r}_{12} \leftarrow T). \end{aligned}$$

Then the invariant expansion of the function  $f$  is finally given in

$$f = \sum_{\substack{l_1 \ l_2 \ l \\ m_1 \ m_2}} f_{m_1 m_2}^{l_1 l_2 l}(|\vec{r}_{12}|) \phi_{m_1 m_2}^{l_1 l_2 l}(1 \leftarrow T, 2 \leftarrow T, \vec{r}_{12} \leftarrow T)$$

The molecular symmetry of the molecules making up the fluid imposes additional constraints on the above expansion. In the case of linear molecules (including dipolar hard spheres as a special case)

$m_1 = m_2 = 0$  and so the expansion is done effectively in spherical harmonics for the three directions  $1 \leftarrow T$ ,  $2 \leftarrow T$ ,  $\vec{r}_{12} \leftarrow T$ .

Several changes in notation will now be introduced: the subscripts

$m_1$  and  $m_2$  (both zero for this thesis) are superfluous and so omitted; the angular dependence will be given by  $\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r$  rather than by Jepsen and Friedman's notation  $1 \leftarrow T, 2 \leftarrow T, \vec{r}_{12} \leftarrow T$ .

These bookkeeping changes then give the invariant expansion of  $f$  in Blum and Torruella's (1972) form as

$$f = \sum_{mn\ell} f^{mn\ell}(|\vec{r}|) \phi^{mn\ell}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) \quad (5a)$$

where

$$\begin{aligned} \phi^{mn\ell}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) \\ = \sum_{\mu\nu} \begin{pmatrix} m & n & \ell \\ \mu & \nu & -\mu-\nu \end{pmatrix} D_{0\mu}^m(\vec{\Omega}_1) D_{0\nu}^n(\vec{\Omega}_2) \\ \times D_{0-\mu-\nu}^{\ell}(\vec{\Omega}_r) \end{aligned} \quad (5b)$$

and

$$D_{0m}^{\ell}(\vec{\Omega}) = (4\pi/(2\ell+1))^{\frac{1}{2}} Y_{\ell m}(\theta, \phi).$$

For example, the dipole-dipole intermolecular potential with a hard sphere cut-off can be reformulated as

$$\begin{aligned} V(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) \\ = V^{000}(|\vec{r}|) \phi^{000}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) \\ + V^{112}(|\vec{r}|) \phi^{112}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r), \end{aligned} \quad (6a)$$

where

$$V^{000}(|\vec{r}|) = \begin{cases} \infty & \text{if } |\vec{r}| < R_{\alpha\beta} \\ 0 & \text{if } |\vec{r}| \geq R_{\alpha\beta} \end{cases} \quad (6b)$$

and

$$V^{112}(|\vec{r}|) = \frac{\sqrt{60} \beta m_\alpha m_\beta}{|\vec{r}|^3} \quad (6c)$$

It is straightforward to show from equation (5b) that

$$\phi^{000} = 1$$

and

$$\phi^{112} = D(\vec{\mathcal{L}}_1, \vec{\mathcal{L}}_2, \vec{\mathcal{L}}_r) / \sqrt{60}.$$

Indeed, any electrostatic interaction between multipoles can be expressed in the form of equation (5a) above. Explicitly (Blum, 1972),

$$V(\vec{r}_1, \vec{\mathcal{L}}_1, \vec{r}_2, \vec{\mathcal{L}}_2) = \sum_{mnl} \frac{v_{\mu\nu}^{mnl}}{|\vec{r}|^{l+1}} \phi_{\mu\nu}^{mnl}(\vec{\mathcal{L}}_1, \vec{\mathcal{L}}_2, \vec{\mathcal{L}}_r),$$

where  $v_{\mu\nu}^{mnl}$  is related to the product of the magnitudes of the interacting multipoles. Obviously if the order of multipoles present in each molecule is finite (e.g.  $m = n = 2$  for the quadrupole), then the expansion is finite.

In the next Section, it will be seen that such an expansion for any pair distribution function has a finite number of terms in the Mean Spherical Approximation if "polarization effects" are neglected. The invariance used above also ensures that the basis sets in  $r$  and  $k$  spaces are identical (Blum and Torruella, 1972). These properties will then be used to solve the Ornstein-Zernike equation for dipolar fluid mixtures in the Mean Spherical Approximation. The invariant expansions are quite general

techniques and independent of the Mean Spherical Approximation.

### 3. Invariant Expansion of the Correlation Functions

#### 3.1 Introduction

Originally, Jepsen and Friedman (1963) had employed invariant expansions to calculate cluster expansions for dipolar forces. Later, Steele (1963) gave a general treatment of the statistical mechanical properties in terms of these expansions for the relevant correlation functions. However, the relative coordinates in the  $\vec{r}_{12}$  frame of reference were utilized in such treatments. The fully invariant expansion over rotations in an arbitrary coordinate system was given by Wertheim (1971) for a dipolar hard sphere fluid. An analytic solution was given for the Ornstein-Zernike equation. This technique has since been generalized by Blum (1972, 1973) to arbitrarily shaped molecules interacting via various electrostatic multipole potentials. The appealing feature of Blum's expansion is the reduction of the multi-dimensional integrals in the Ornstein-Zernike equation to a set of coupled algebraic equations in  $k$  space. Within the Mean Spherical Approximation, the two approaches are equivalent and the exact correspondence will be detailed later.

#### 3.2 Reformulation of the Ornstein-Zernike Equation using Invariant Expansions for the Correlation Functions

It is instructive to consider the invariant expansion of the pair distribution function for a single component fluid, and generalize these results later for mixtures. The invariance of the pair distribution function  $g(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  (to rotations

and translations of the standard Cartesian coordinate system S)

implies that if it can be expanded, then the expansion is

invariant so that equation (5a) becomes

$$g(\vec{r}_1, \vec{r}_2, \vec{r}_1, \vec{r}_2) = \sum_{mnl} g^{mnl}(|\vec{r}_1|) \phi^{mnl}(\vec{r}_1, \vec{r}_2, \vec{r}_r) \quad (7)$$

Here the summation indexes m and n are nonnegative integers

$$0 \leq m, n \leq \infty \quad \text{and } l \text{ is restricted to the range} \\ |m-n| \leq l \leq m+n \quad \text{by equation (5b). Then } g(\vec{r}_1, \vec{r}_2, \vec{r}_1, \vec{r}_2)$$

is exactly detailed by the infinite set of radial coefficients

$g^{mnl}(|\vec{r}_1|)$ . However the orthogonality of the  $\phi$ 's implies that

the mechanical thermodynamic properties (internal energy and

pressure) are determined by only a finite number of radial

coefficients. The type and number of these coefficients are

determined by the corresponding terms in the finite expansion of

the intermolecular pair potential. For a fluid of nonpolarizable

dipolar hard spheres the invariant expansion is given by the one

component analogue of equation (6), namely

$$u(\vec{r}_1, \vec{r}_2, \vec{r}_1, \vec{r}_2) = u^{000}(|\vec{r}_1|) \phi^{000}(\vec{r}_1, \vec{r}_2, \vec{r}_r) + u^{112}(|\vec{r}_1|) \phi^{112}(\vec{r}_1, \vec{r}_2, \vec{r}_r),$$

where  $u^{000}$  and  $u^{112}$  are given by equations (6b) and (6c) leaving

out the  $\alpha, \beta$  subscripts. From equations (11) and (12) of Chapter 1,

the internal energy and pressure of a fluid of dipolar hard spheres

are given by

$$E = E_{\text{kinetic}} + \frac{\rho^2}{2} \int d\vec{r} u^{000}(r) g^{000}(r) \\ + \frac{\rho^2}{90} \int d\vec{r} u^{112}(r) g^{112}(r)$$

and

$$p = \rho kT - \frac{\rho^2}{6} \int d\vec{r} \, r \frac{\partial u^{000}}{\partial r} g^{000}(r) \\ - \frac{\rho^2}{540} \int d\vec{r} \, r \frac{\partial u^{112}}{\partial r} g^{112}(r) .$$

From these equations, it is seen that the thermodynamical properties can be written as an ideal gas term arising from kinetic motion of the molecules only, a hard sphere contribution and a dipolar contribution. All are evaluated at the same density and temperature. These equations would describe the pressure and internal energy exactly if the  $g^{000}$  and  $g^{112}$  were determined accurately.

A careful study of the Ornstein-Zernike equation gives the exact equations which must then be solved to obtain  $g^{000}$  and  $g^{112}$ . Blum and Torruella (1972) have carried out such an investigation using a complete expansion for the indirect and direct correlation functions  $h(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$  and  $c(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$ , respectively. The Fourier transforms,  $h^{mnl}(k)$  and  $c^{mnl}(k)$ , of the radial coefficients are given in the Ornstein-Zernike equation in k-space by (Blum, 1972)

$$h^{mnl}(k) - c^{mnl}(k) \\ = \rho \sum_{n_1 l_1 l_2} Z_{m n n_1}^{l_2 l_1 l} h^{m n_1 l_1}(k) c^{n_1 n l_2}(k) \quad (8)$$

where

$$Z_{m n n_1}^{l_2 l_1 l} = (-)^{m+n+n_1} \left| \frac{2l+1}{2n_1+1} \right| \left\{ \begin{matrix} l_2 & l_1 & l \\ m & n & n_1 \end{matrix} \right\} \left\{ \begin{matrix} l_2 & l_1 & l \\ 0 & 0 & 0 \end{matrix} \right\}$$

and  $\left\{ \right\}$  denote the 6-j symbol (Edmonds, 1974), and the coefficients  $h^{mnl}(k)$  and  $c^{mnl}(k)$  are the Hankel transforms of the radial coefficients  $h^{mnl}(r)$  and  $c^{mnl}(r)$ , given by

$$h^{mnl}(k) = 4\pi i^l \int_0^\infty dr \, r^2 j_l(kr) h^{mnl}(r)$$

and

$$c^{mnl}(k) = 4\pi i l \int_0^\infty dr r^2 j_l(kr) c^{mnl}(r) .$$

It follows from this equation that the  $h^{000}$  term is coupled to an infinite set of the type  $h^{0n_1n_1}$  where  $0 \leq n_1 \leq \infty$ . This can be seen from setting  $m = n = l = 0$  and observing the 3-j and 6-j symbols are nonzero only for  $l_2 = l_1 = n_1$ . Then explicitly

$$\begin{aligned} h^{000}(k) - c^{000}(k) \\ = \rho \sum_{n_1=0}^{\infty} Z_{00n_1}^{n_1n_10} h^{0n_1n_1}(k) c^{n_10n_1}(k) . \end{aligned} \quad (9)$$

Corresponding operations show that the  $h^{112}$  term is coupled to an infinite set of the types  $h^{1n_1|n_1-1|}$ ,  $h^{1n_1n_1}$  and  $h^{1n_1n_1+1}$  where  $0 \leq n_1 \leq \infty$ . This is shown explicitly in

$$\begin{aligned} h^{112}(k) - c^{112}(k) \\ = \rho \sum_{n_1=0}^{\infty} \sum_{l_1 l_2} Z_{11n_1}^{l_2 l_1 2} h^{1n_1 l_1}(k) c^{n_1 l_2}(k) \end{aligned} \quad (10)$$

where  $|n_1-1| \leq l_1, l_2 \leq n_1+1$ , and  $l_1 + l_2$  is even.

Although the above results for the coupling of the various  $h^{mnl}(k)$  with either  $h^{000}(k)$  or  $h^{112}(k)$  are based on the form of the Ornstein-Zernike equation in  $k$ -space, the conclusions are the same in  $r$ -space. This follows from the fact that the coupling of the coefficients  $h^{mnl}(k)$  to  $h^{rst}(k)$  is given by the integral  $\int d\vec{\Omega}_3 \phi^{mnl}(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) \phi^{rst}(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K)$ . In  $r$ -space, the coupling is preserved since the  $\phi^{mnl}$ 's are invariant to Fourier transform (Blum 1972; Wertheim, 1971). However, the details of the coupling scheme in  $r$ -space are far more complicated, and this will be discussed later.

Returning to the Ornstein-Zernike equation in  $k$ -space, a closure to the hierarchy of equations (9) and (10) is provided by neglecting certain Fourier coefficients  $h^{mnl}(k)$ . Such a closure scheme is equivalent to omitting the angular function  $\phi^{mnl}$  from the expansion of the distribution function. The Mean Spherical Approximation ensures the presence of  $\phi^{000}$  and  $\phi^{112}$  in the expansions for the direct and indirect correlation functions.

In order to classify the types of terms  $h^{mnl}(k)$  that are to be omitted, it is necessary to look at the convolutions of an arbitrary  $\phi^{mnl}$  with  $\phi^{000}$  and  $\phi^{112}$ . Integrating the respective products over  $\vec{\Omega}_3$  gives

$$\int d\vec{\Omega}_3 \phi^{000}(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) \phi^{mnl}(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) = \delta_{m0} \phi^{0nl}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) \quad (11a)$$

and

$$\int d\vec{\Omega}_3 \phi^{112}(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) \phi^{mnl}(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) = \delta_{m1} \sum_j \begin{pmatrix} 2 & l & j \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} j & n & 1 \\ 1 & 2 & l \end{Bmatrix} \phi^{1nl}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K). \quad (11b)$$

Projecting onto  $\phi^{000}$  in the first of these equations, the only nonzero contribution arises for  $m = n = l = 0$ . This means that the following equation can be written down

$$h^{000}(k) - c^{000}(k) = \rho h^{000}(k) c^{000}(k). \quad (12)$$

The projection of the second equation onto  $\phi^{112}$  gives the coupling between  $h^{110}(k)$  and  $h^{112}(k)$ . The corresponding coupling between  $h^{111}(k)$  and  $h^{112}(k)$  vanishes through the corresponding 3-j symbol becoming zero. These operations give the

following equation for the  $h^{12}(k)$  coefficient

$$\begin{aligned}
 h^{12}(k) - c^{12}(k) \\
 = \frac{\rho}{3\sqrt{3}} \left\{ \frac{1}{\sqrt{10}} h^{12}(k) c^{12}(k) + h^{110}(k) c^{12}(k) \right. \\
 \left. + h^{12}(k) c^{110}(k) \right\}. \quad (13a)
 \end{aligned}$$

From this equation it appears that  $\phi^{110}$  is an angular function which couples with  $\phi^{12}$  under convolution to give a nonzero contribution to the  $\phi^{12}$  dependence. The convolution properties of  $\phi^{110}$  are then important in order to determine the equation for  $h^{110}(k)$ . It is easily shown that

$$\begin{aligned}
 \int d\vec{\Omega}_3 \phi^{110}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_3) \phi^{mn\ell}(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) \\
 = -\frac{\delta_{m1}}{\sqrt{3}} \phi^{1n\ell}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)
 \end{aligned}$$

and the corresponding equation for the Fourier coefficients is

$$\begin{aligned}
 h^{110}(k) - c^{110}(k) \\
 = \frac{\rho}{3\sqrt{3}} \left\{ h^{110}(k) c^{110}(k) - \frac{1}{5} h^{12}(k) c^{12}(k) \right\} \quad (13b)
 \end{aligned}$$

### 3.3 The Choice of Rotational Invariants for the Mean Spherical Approximation

It appears from the above analysis leading to equations (12), (13a) and (13b) that the basis set  $\phi^{000}$ ,  $\phi^{110}$  and  $\phi^{12}$  can be used to project a closed set of equations from the infinite set of equations (8). The closure is a natural consequence of the three basis functions forming a closed set under convolution over  $\vec{\Omega}_3$  in  $k$ -space. Wertheim (1971) suggested that such a set of functions might then be used in an Ansatz to determine the thermodynamic and dielectric properties of a fluid of dipolar hard spheres, using the solution for  $h^{12}$  as given via the coupled equation for

$h^{112}$  and  $h^{110}$  only. In such an approach, the correlation functions are given by the first few terms of the infinite expansion, equation (7), as

$$\begin{aligned}
 g(\vec{r}_1, \vec{r}_2, \vec{r}_2) &= g^{000}(r_{12}) \phi^{000}(\vec{r}_1, \vec{r}_2, \vec{r}_r) \\
 &+ g^{110}(r_{12}) \phi^{110}(\vec{r}_1, \vec{r}_2, \vec{r}_r) \\
 &+ g^{112}(r_{12}) \phi^{112}(\vec{r}_1, \vec{r}_2, \vec{r}_r) \quad , \quad (14a)
 \end{aligned}$$

and

$$\begin{aligned}
 c(\vec{r}_1, \vec{r}_2, \vec{r}_2) &= c^{000}(r_{12}) \phi^{000}(\vec{r}_1, \vec{r}_2, \vec{r}_r) \\
 &+ c^{110}(r_{12}) \phi^{110}(\vec{r}_1, \vec{r}_2, \vec{r}_r) \\
 &+ c^{112}(r_{12}) \phi^{112}(\vec{r}_1, \vec{r}_2, \vec{r}_r) \quad . \quad (14b)
 \end{aligned}$$

As mentioned previously, the Mean Spherical Approximation gives the following boundary conditions in terms of the  $h^{mnl}(r)$  and  $c^{mnl}(r)$  as

$$g^{000}(r) = 0 \quad \text{if} \quad r < R \quad (15a)$$

and

$$c^{112}(r) = \beta m^2 r^{-3} \quad \text{if} \quad r \geq R \quad . \quad (15b)$$

From these equations it can be seen that  $\phi^{000}$  and  $\phi^{112}$  must be included in the expansion of the correlation functions. This is obvious from the thermodynamic equations involving  $h^{000}$  and  $h^{112}$  .

However the projection of the total angular dependence of the exact  $g$  and  $c$  onto the subspace spanned by  $\phi^{ooo}$ ,  $\phi^{110}$  and  $\phi^{112}$  is an approximation. In order to make some comment on Wertheim's Ansatz, equations (14), in the Mean Spherical Approximation it is necessary to examine the physical interpretation given to the angular dependences not included in such a projection onto the subspace  $(\phi^{ooo}, \phi^{110}, \phi^{112})$ . This is most conveniently achieved by comparison of equations describing the exact  $h^{ooo}(k)$  and  $h^{112}(k)$  and the Mean Spherical Approximation equations, i.e., comparison of equations (9) and (12), and (10) and (13a). The latter gives the neglect of two types of terms. This classification is based on the order of the  $m\ n\ l$  superscripts in comparison to the  $112$  set of superscripts. Coefficients lower in order (yet higher in order than the lowest order  $ooo$ ) than  $112$  which were neglected in the Mean Spherical Approximation equations (Wertheim, 1971) were  $h^{o11}$  and  $h^{101}$  in equation (12), and  $h^{101}$  and  $h^{111}$  in equation (13a). Coefficients higher in order than  $112$  included  $h^{on n}$  and  $h^{non}$  for  $n \geq 2$  in equation (12) and  $h^{1 n n-1}$ ,  $h^{1 n n}$ ,  $h^{1 n n+1}$  for  $n \geq 2$  in equation (13a). The low order class of terms (excluding  $h^{111}$ ) is the set of coefficients associated with the angular dependence of a dipole-hard core correlation. Similarly, the higher order coefficients represent correlations between dipole-higher order multipole interactions in the fluid. Such correlations are assumed to be negligible in Wertheim's solution of the Mean Spherical Approximation for a dipolar fluid. Indeed, Blum has confirmed (Blum, 1974) that within the linear approximation of the Mean Spherical Approximation a dipolar interaction cannot induce a quadrupole correlation (configuration). Thus these heuristic arguments suggest that Wertheim's choice of the three basis functions  $\phi^{ooo}$ ,

$\phi^{110}$  and  $\phi^{112}$  in the Ansatz involves the assumption that polarization phenomena involving dipole-hard sphere and dipole-induced multipole interactions are negligible.

The Monte-Carlo studies of 864 dipolar hard spheres (Verlet and Weis, 1974) has confirmed Wertheim's Ansatz for the Monte-Carlo generated radial distribution function. Although the projection of the Monte-Carlo radial distribution function onto the subspace not spanned by  $(\phi^{000}, \phi^{110}, \phi^{112})$  is quite small, the actual radial coefficients  $h^{110}$  and  $h^{112}$  are considerably different from those given by the Mean Spherical Approximation. From Figures 2 and 3 of the paper of Verlet and Weis, it can be seen that the results of the Mean Spherical Approximation considerably underestimate those of the Monte-Carlo runs. This underestimation of correlations given by attractive forces was predicted by Andersen (1975) for the Mean Spherical Approximation.

In summary, the use of the complete set of rotational invariants  $\phi^{mnl}$  in expanding the direct and indirect correlation functions is impractical. However the Mean Spherical Approximation can be interpreted as truncating such a complete set of  $\phi^{mnl}$ 's to the highest order of  $\phi^{112}$ . Such a collection of rotational functions implicitly assumes the negligibility of polarization effects (e.g., quadrupole symmetry being induced throughout the fluid purely from dipole forces). The rest of the truncated basis set is chosen so that dipole-hard core symmetries are also neglected. Within these two assumptions, Wertheim's equations for the correlation coefficients  $h^{000}$  and  $h^{112}$  can be derived from the exact equations

of Blum (1972) for  $h^{ooo}$  and  $h^{''2}$ . The problem of hard core polarization by a dipole should be looked at in the future by including more basis functions of the type  $\phi^{'01}$ .

At present, Wertheim's Ansatz for the truncated invariant expansion of  $h$  and  $c$  in the pure component fluid, equation (14), will be extended to the expansion of the corresponding correlation functions for multicomponent systems.

Thus we will solve the Ornstein-Zernike equation (equation (21) of Chapter 1) subject to the closure rules (equation (22) of Chapter 1) using these truncated expansions for the correlation functions. In the remainder of this thesis, the Mean Spherical Approximation refers to the solution so obtained. It must be stressed that this definition of the Mean Spherical Approximation was implicitly adopted by Wertheim (1971) in his classic paper on the subject.

### 3.4 The Decoupling of the Ornstein-Zernike Equation in the Mean Spherical Approximation

At this point in the presentation, a change in notation is required in order to directly apply Wertheim's approach of solving the Ornstein-Zernike equation in  $r$ -space rather than in  $k$ -space. In the notation employed by Wertheim (1971), the angular functions  $\phi^{ooo}$ ,  $\phi^{''0}$  and  $\phi^{''2}$  are called  $I(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$ ,  $\Delta(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$  and  $D(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$ , respectively. The exact relationship is detailed in the following equations

$$I(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}_{12}) = \phi^{000} = 1,$$

$$\Delta(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}_{12}) = -\sqrt{3} \phi^{110} = \vec{S}_1(\vec{\Omega}_1) \cdot \vec{S}_2(\vec{\Omega}_2),$$

and

$$D(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}_{12}) = 2\sqrt{15} \phi^{112} = \vec{S}_1(\vec{\Omega}_1) \cdot \left( 3 \frac{\vec{r}_{12} \vec{r}_{12}}{|\vec{r}_{12}|^2} - \mathbb{U} \right) \cdot \vec{S}_2(\vec{\Omega}_2).$$

The direct and indirect correlation functions  $c_{\alpha\beta}$  and  $h_{\alpha\beta}$  are then expanded in terms of  $I$ ,  $\Delta$  and  $D$  and undetermined radial coefficients. It should be noted these angular functions are species independent, allowing the reduction of the Ornstein-Zernike equation to a set of simpler equations for the unknown radial dependence. Before giving any explicit forms, it is again appropriate to point out the symmetry conditions involved.

1. For a homogeneous fluid the correlation functions are translationally invariant. Then the  $\vec{r}_1, \vec{r}_2$  dependence is compounded as  $\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$ . For example

$$h_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = h_{\alpha\beta}(\vec{r}_{12}, \vec{\Omega}_1, \vec{\Omega}_2).$$

This is usually expressed by saying the  $h_{\alpha\beta}$  are independent of choice of origin.

2. Isotropy asserts that the functions be rotationally invariant. In other words  $h_{\alpha\beta}(\vec{r}_{12}, \vec{\Omega}_1, \vec{\Omega}_2)$  should transform as a scalar quantity for arbitrary rotations of the reference frame.

3. The Mean Spherical Approximation gives the highest order angular dependence in  $c_{\alpha\beta}(\vec{r}_{12}, \vec{\Omega}_1, \vec{\Omega}_2)$  as  $D(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$ , whilst the hard core nature of  $h_{\alpha\beta}(\vec{r}_{12}, \vec{\Omega}_1, \vec{\Omega}_2)$  is represented by  $I(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$ , unity. Higher order symmetries as would be provided for by polarization of the hard core by dipole fields, are neglected. From the Ornstein-Zernike equation, it is evident that the correlation functions are of the same order with respect to angular dependence. Since  $h_{\alpha\beta}$  and  $c_{\alpha\beta}$  have equivalent representation (occurring to the same degree) in the Ornstein-Zernike equation, the highest order angular dependence known for  $c_{\alpha\beta}$  is also that for  $h_{\alpha\beta}$ , namely  $D(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$ .

The explicit forms are then given as

$$h_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = h_{\alpha\beta}^S(r_{12}) I(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) + h_{\alpha\beta}^A(r_{12}) \Delta(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) + h_{\alpha\beta}^D(r_{12}) D(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) \quad (16)$$

$$c_{\alpha\beta}(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = c_{\alpha\beta}^S(r_{12}) I(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) + c_{\alpha\beta}^A(r_{12}) \Delta(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) + c_{\alpha\beta}^D(r_{12}) D(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}). \quad (17)$$

where  $r_{12} = |\vec{r}_2 - \vec{r}_1|$ . The tensorial nature of  $D(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$  does not allow straight-forward substitution of these expansions into the Ornstein-Zernike equation. If this is done the generalized convolution  $\int d\vec{r}_3 \int d\vec{\Omega}_3$  involves unnecessary tensorial properties in the spatial convolution operation. This is removed by defining operators closely associated with the angular functions, and then carrying out the convolution (for details, see Appendix 2). Following Wertheim's technique, the differential operators

$\mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$ ,  $\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$  and  $\mathcal{I}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$  are defined in

$$\begin{aligned}\mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) &= \vec{S}_1(\vec{\Omega}_1) \cdot (3 \vec{\nabla} \vec{\nabla} - \underline{\underline{U}} \nabla^2) \cdot \vec{S}_2(\vec{\Omega}_2) \\ \Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) &= \vec{S}_1(\vec{\Omega}_1) \cdot \vec{S}_2(\vec{\Omega}_2) \nabla^2 \\ \mathcal{I}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) &= 1\end{aligned}\quad (18)$$

The motivation of using these differential operators can be found in the solution of the Ornstein-Zernike equation in k-space. The details are given extensively in Appendix 2.

In this operational formalism, equations (16) and (17) become

$$\begin{aligned}h_{\alpha\beta}(\vec{r}_{12}, \vec{\Omega}_1, \vec{\Omega}_2) &= \mathcal{I}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) H_{\alpha\beta}^S(r_{12}) + \Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) H_{\alpha\beta}^\Delta(r_{12}) \\ &\quad + \mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) H_{\alpha\beta}^D(r_{12})\end{aligned}\quad (19)$$

$$\begin{aligned}C_{\alpha\beta}(\vec{r}_{12}, \vec{\Omega}_1, \vec{\Omega}_2) &= \mathcal{I}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) C_{\alpha\beta}^S(r_{12}) + \Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) C_{\alpha\beta}^\Delta(r_{12}) \\ &\quad + \mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) C_{\alpha\beta}^D(r_{12}).\end{aligned}\quad (20)$$

Note that it immediately follows from equation (18) that

$$H_{\alpha\beta}^S(r_{12}) = h_{\alpha\beta}^S(r_{12}) \quad \text{and} \quad C_{\alpha\beta}^S(r_{12}) = c_{\alpha\beta}^S(r_{12}).$$

The relationship between the two sets of anisotropic radial coefficients is given in differential or integral equations. In the simpler case of the  $\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r})$  consider the following equation for  $\psi_{\alpha\beta}$  ( $= h_{\alpha\beta}^\Delta$  or  $c_{\alpha\beta}^\Delta$ ) and its relationship to  $\Psi_{\alpha\beta}$  ( $= H_{\alpha\beta}^\Delta$  or  $C_{\alpha\beta}^\Delta$ ),

$$\begin{aligned}\psi_{\alpha\beta}(r) \Delta(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}) &= \Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}) \Psi_{\alpha\beta}(r) \\ &= \Delta(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}) \nabla^2 \Psi_{\alpha\beta}(r) .\end{aligned}\quad (21)$$

Since the directions are arbitrary this reduces to

$$\begin{aligned}\psi_{\alpha\beta}(r) &= \nabla^2 \Psi_{\alpha\beta}(r) \\ &= \frac{d^2 \Psi_{\alpha\beta}}{dr^2} + \frac{2}{r} \frac{d \Psi_{\alpha\beta}}{dr} ,\end{aligned}\quad (22)$$

where  $\nabla^2 = \frac{1}{r^2} \frac{d}{dr} (r^2 \frac{d}{dr})$  operates on functions which are dependent on  $r$  rather than  $\vec{r}$ . It will be seen that the natural variables in the decoupling of the Ornstein-Zernike equation are

$\nabla^2 \Psi_{\alpha\beta}(r)$ , eliminating the need for the inverse relationship.

An alternative proof of equation (22) is given in terms of the Hankel transforms of  $\psi(r)$  and  $\Psi(r)$  in Appendix 2.

For the  $D_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r})$  the direct route is via the matrix representation of the differential tensor  $3 \vec{\nabla} \vec{\nabla} - \nabla^2$ . From the Cartesian coordinates  $\vec{r} = (x_1, x_2, x_3)$  it can be shown from simple chain rule differentiation that

$$\begin{aligned}\frac{\partial}{\partial x_\alpha} &= \frac{x_\alpha}{r} \frac{\partial}{\partial r} \\ \frac{\partial^2}{\partial x_\alpha^2} &= \frac{x_\alpha^2}{r^2} \frac{\partial^2}{\partial r^2} + \frac{(r^2 - x_\alpha^2)}{r^3} \frac{\partial}{\partial r}\end{aligned}$$

$$\alpha = 1, 2, 3 .$$

These derivatives are then used to simplify the matrix

$$3\vec{\nabla}\vec{\nabla}-\underline{\underline{U}}\nabla^2=\begin{bmatrix} 2\frac{\partial^2}{\partial x_1^2}-\frac{\partial^2}{\partial x_2^2}-\frac{\partial^2}{\partial x_3^2} & 3\frac{\partial^2}{\partial x_1\partial x_2} & 3\frac{\partial^2}{\partial x_1\partial x_3} \\ 3\frac{\partial^2}{\partial x_2\partial x_1} & 2\frac{\partial^2}{\partial x_2^2}-\frac{\partial^2}{\partial x_1^2}-\frac{\partial^2}{\partial x_3^2} & 3\frac{\partial^2}{\partial x_2\partial x_3} \\ 3\frac{\partial^2}{\partial x_3\partial x_1} & 3\frac{\partial^2}{\partial x_3\partial x_2} & 2\frac{\partial^2}{\partial x_3^2}-\frac{\partial^2}{\partial x_1^2}-\frac{\partial^2}{\partial x_2^2} \end{bmatrix}$$

$$=\begin{bmatrix} \frac{3x_1^2}{r^2}-1 & \frac{3x_1x_2}{r^2} & \frac{3x_1x_3}{r^2} \\ \frac{3x_2x_1}{r^2} & \frac{3x_2^2}{r^2}-1 & \frac{3x_2x_3}{r^2} \\ \frac{3x_3x_1}{r^2} & \frac{3x_3x_2}{r^2} & \frac{3x_3^2}{r^2}-1 \end{bmatrix}\left(\frac{d^2}{dr^2}-\frac{1}{r}\frac{d}{dr}\right)$$

$$=\underline{\underline{T}}(\hat{\vec{r}})\left(\frac{d^2}{dr^2}-\frac{1}{r}\frac{d}{dr}\right). \quad (23)$$

Performing the contraction with  $\vec{S}_1(\vec{\Omega}_1)$  and  $\vec{S}_2(\vec{\Omega}_2)$  then

gives

$$D_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{\vec{r}}) = \vec{S}_1(\vec{\Omega}_1) \cdot \underline{\underline{T}}(\hat{\vec{r}}) \cdot \vec{S}_2(\vec{\Omega}_2) \left(\frac{d^2}{dr^2}-\frac{1}{r}\frac{d}{dr}\right). \quad (24)$$

Consider the operation of  $\mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r})$  on some function  $\Phi(r)$ . The following equality is true

$$\mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}) \Phi(r) = \mathcal{D}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}) \phi(r)$$

for

$$\phi(r) = \frac{d^2 \Phi(r)}{dr^2} - \frac{1}{r} \frac{d\Phi(r)}{dr} . \quad (25)$$

Also this equation can be integrated to give  $\Phi(r)$  in terms of  $\phi(r)$ , assuming  $\phi(r) \rightarrow 0$  faster than  $r^{-1}$  as  $r \rightarrow \infty$ :

$$\Phi(r) = \frac{1}{2} \int_r^\infty dx \phi(x) (x^2 - r^2)/x . \quad (26)$$

In summary  $H_{\alpha\beta}^D(r)$ ,  $C_{\alpha\beta}^D(r)$  can be differentiated to obtain  $h_{\alpha\beta}^D(r)$ ,  $c_{\alpha\beta}^D(r)$  as described in deriving  $\phi(r)$  from  $\Phi(r)$ . Similarly  $H_{\alpha\beta}^A(r)$ ,  $C_{\alpha\beta}^A(r)$  are related to  $h_{\alpha\beta}^A(r)$ ,  $c_{\alpha\beta}^A(r)$  in the same way as  $\Psi(r)$  to  $\psi(r)$ .

The operational expressions, equations (19) and (20), for  $c_{\alpha\beta}$  and  $h_{\alpha\beta}$  are now substituted into the Ornstein-Zernike equation. In fact the differential forms of  $\mathcal{D}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r})$  and  $\Delta(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r})$  allow the angular convolution over  $\vec{\Omega}_3$  to be performed. Indeed, this approach removes any tensorial factors which would have otherwise appeared in the remaining spatial convolution over  $\vec{r}_3$ . Wertheim has shown, furthermore, that these operators form a closed set under the  $\vec{\Omega}_3$  convolution. This property is also true in the multicomponent case presented here. The details are given in terms of the angular convolution AB which is defined as

$$AB = \int d\vec{\Omega}_3 A(\vec{r}_{13}, \vec{\Omega}_1, \vec{\Omega}_3) B(\vec{r}_{32}, \vec{\Omega}_3, \vec{\Omega}_2) . \quad (27)$$

The convolution rules can be written down from the simpler integrals

$$\int d\vec{\Omega}_3 \vec{s}_3(\vec{\Omega}_3) = 0$$

$$\int d\vec{\Omega}_3 \vec{s}_3(\vec{\Omega}_3) \vec{s}_3(\vec{\Omega}_3) = \frac{4\pi}{3} \mathbf{U}$$

as

$$I_{op} I_{op} = 4\pi I_{op}$$

$$\begin{aligned} I_{op} \Delta_{op} &= \Delta_{op} I_{op} \\ &= 0 \end{aligned}$$

$$\begin{aligned} I_{op} D_{op} &= D_{op} I_{op} \\ &= 0 \end{aligned}$$

$$\Delta_{op} \Delta_{op} = \frac{4\pi}{3} \Delta_{op} \nabla^2$$

$$\begin{aligned} \Delta_{op} D_{op} &= D_{op} \Delta_{op} \\ &= \frac{4\pi}{3} D_{op} \nabla^2 \end{aligned}$$

$$D_{op} D_{op} = \frac{4\pi}{3} (D_{op} + 2 \Delta_{op}) \nabla^2 . \quad (28)$$

The details are given in Appendix 3.

Thus using the above rules in the Ornstein-Zernike equation (see Chapter 1, equation (21)), one obtains

$$\begin{aligned}
 & I_{op}(\vec{J}_1, \vec{J}_2, \hat{\vec{r}}_{12}) \left[ H_{\alpha\beta}^s(r_{12}) - C_{\alpha\beta}^s(r_{12}) - \sum_{\gamma} \rho_{\gamma} H_{\alpha\gamma}^s * C_{\gamma\beta}^s \right] \\
 & + \Delta_{op}(\vec{J}_1, \vec{J}_2, \hat{\vec{r}}_{12}) \left[ H_{\alpha\beta}^{\Delta}(r_{12}) - C_{\alpha\beta}^{\Delta}(r_{12}) \right. \\
 & \quad \left. - \sum_{\gamma} \frac{\rho_{\gamma}}{3} \nabla^2 (2 H_{\alpha\gamma}^D * C_{\gamma\beta}^D + H_{\alpha\gamma}^{\Delta} * C_{\gamma\beta}^{\Delta}) \right] \\
 & + D_{op}(\vec{J}_1, \vec{J}_2, \hat{\vec{r}}_{12}) \left[ H_{\alpha\beta}^D(r_{12}) - C_{\alpha\beta}^D(r_{12}) \right. \\
 & \quad \left. - \sum_{\gamma} \frac{\rho_{\gamma}}{3} \nabla^2 (H_{\alpha\gamma}^D * C_{\gamma\beta}^D + H_{\alpha\gamma}^{\Delta} * C_{\gamma\beta}^D + H_{\alpha\gamma}^D * C_{\gamma\beta}^{\Delta}) \right] \\
 & = 0 .
 \end{aligned} \tag{29}$$

Here the spatial convolution over  $\vec{r}_3$  is symbolized in

$$H * C = \int d\vec{r}_3 H(r_{13}) C(r_{32}) . \tag{30}$$

The angular properties of  $I(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r})$ ,  $\Delta(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r})$  and  $D(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r})$ , in particular their orthogonality, are carried over in the respective operators (for details see Appendix 4). Using the orthogonality relations with respect to  $\vec{\Omega}_1$  and  $\vec{\Omega}_2$ , equation (29) can be reduced to a set of three Ornstein-Zernike-like equations. These are

$$I_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) [H_{\alpha\beta}^S(r_{12}) - C_{\alpha\beta}^S(r_{12}) - \sum_{\gamma} \rho_{\gamma} H_{\alpha\gamma}^S * C_{\gamma\beta}^S] = 0 \quad (31)$$

$$\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) [H_{\alpha\beta}^A(r_{12}) - C_{\alpha\beta}^A(r_{12}) - \sum_{\gamma} \frac{\rho_{\gamma}}{3} \nabla^2 (2H_{\alpha\gamma}^D * C_{\gamma\beta}^D + H_{\alpha\gamma}^A * C_{\gamma\beta}^A)] = 0 \quad (32)$$

$$D_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12}) [H_{\alpha\beta}^D(r_{12}) - C_{\alpha\beta}^D(r_{12}) - \sum_{\gamma} \frac{\rho_{\gamma}}{3} \nabla^2 (H_{\alpha\gamma}^D * C_{\gamma\beta}^D + H_{\alpha\gamma}^A * C_{\gamma\beta}^D + H_{\alpha\gamma}^D * C_{\gamma\beta}^A)] = 0 \quad (33)$$

Equation (31) is completely independent of equations (32) and (33), and so will be investigated first. Since  $I_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \hat{r}_{12})$  is the identity operator, equation (31) can be rewritten

$$h_{\alpha\beta}^S(r_{12}) = C_{\alpha\beta}^S(r_{12}) + \sum_{\gamma} \rho_{\gamma} \int d\vec{r}_3 h_{\alpha\gamma}^S(r_{13}) C_{\gamma\beta}^S(r_{32}). \quad (34)$$

In order to solve equations (32), (33) and (34) the closure rules of the Mean Spherical Approximation must be given in terms of the radial coefficients  $H_{\alpha\beta}^{\Delta}(r)$ ,  $C_{\alpha\beta}^{\Delta}(r)$  and  $H_{\alpha\beta}^{\text{D}}(r)$ ,  $C_{\alpha\beta}^{\text{D}}(r)$ , and finally  $h_{\alpha\beta}^{\text{S}}(r)$ ,  $c_{\alpha\beta}^{\text{S}}(r)$ . From equation (22) in Chapter 1,

$$\begin{aligned} h_{\alpha\beta}^{\text{S}}(r) &= -1 & \text{for } r < R_{\alpha\beta} \\ C_{\alpha\beta}^{\text{S}}(r) &= 0 & \text{for } r > R_{\alpha\beta}, \end{aligned} \quad (35)$$

$$\begin{aligned} h_{\alpha\beta}^{\Delta}(r) &= 0 & \text{for } r < R_{\alpha\beta} \\ C_{\alpha\beta}^{\Delta}(r) &= 0 & \text{for } r > R_{\alpha\beta}, \end{aligned} \quad (36)$$

and

$$\begin{aligned} h_{\alpha\beta}^{\text{D}}(r) &= 0 & \text{for } r < R_{\alpha\beta} \\ C_{\alpha\beta}^{\text{D}}(r) &= m_{\alpha}m_{\beta} / (KT r^3) & \text{for } r > R_{\alpha\beta}. \end{aligned} \quad (37)$$

In the above  $R_{\alpha\beta} = (R_{\alpha} + R_{\beta})/2$ .

It is well-known that equation (35) is the Percus-Yevick closure rule for hard sphere mixtures (Lebowitz, 1964) and so equations (34) and (35) are the Ornstein-Zernike equation for hard sphere mixtures in the Percus-Yevick approximation. Fortunately Lebowitz (1964) and Baxter (1970) have independently given solutions of such a model. The direct correlation function  $c_{\alpha\beta}^{\text{S}}(r)$  is known exactly in both cases and Baxter has formulated a linear integral equation for  $h_{\alpha\beta}^{\text{S}}(r)$  which can be solved easily by numerical iteration (Perram, 1975).

However equations (32) and (33) are coupled through anisotropic angular terms. Following Wertheim, the equations are simplified by the use of new variables, suggested by the presence of  $\nabla^2$  in the convolution terms. The transformation is suggested by certain operations in  $k$  space which are detailed in Appendix 2.

Defining

$$\hat{h}_{\alpha\beta}^{\Delta}(r) = \nabla^2 H_{\alpha\beta}^{\Delta}(r) \quad (38)$$

$$\hat{h}_{\alpha\beta}^{\mathcal{D}}(r) = \nabla^2 H_{\alpha\beta}^{\mathcal{D}}(r) \quad (39)$$

and similar expressions for  $\hat{c}_{\alpha\beta}^{\Delta}(r)$ ,  $\hat{c}_{\alpha\beta}^{\mathcal{D}}(r)$  equations (32) and (33) can be reformulated as

$$\hat{h}_{\alpha\beta}^{\Delta}(r) = \hat{c}_{\alpha\beta}^{\Delta}(r) + \sum_{\gamma} \frac{\rho_{\gamma}}{3} (2\hat{h}_{\alpha\gamma}^{\mathcal{D}} * \hat{c}_{\gamma\beta}^{\mathcal{D}} + \hat{h}_{\alpha\gamma}^{\Delta} * \hat{c}_{\gamma\beta}^{\Delta}) \quad (40)$$

$$\hat{h}_{\alpha\beta}^{\mathcal{D}}(r) = \hat{c}_{\alpha\beta}^{\mathcal{D}}(r) + \sum_{\gamma} \frac{\rho_{\gamma}}{3} (\hat{h}_{\alpha\gamma}^{\mathcal{D}} * \hat{c}_{\gamma\beta}^{\mathcal{D}} + \hat{h}_{\alpha\gamma}^{\Delta} * \hat{c}_{\gamma\beta}^{\mathcal{D}} + \hat{h}_{\alpha\gamma}^{\mathcal{D}} * \hat{c}_{\gamma\beta}^{\Delta}) \quad (41)$$

From equation (22) it follows  $\hat{h}_{\alpha\beta}^{\Delta}(r) = h_{\alpha\beta}^{\Delta}(r)$  and  $\hat{c}_{\alpha\beta}^{\Delta}(r) = c_{\alpha\beta}^{\Delta}(r)$ .

Using equation (26) for  $H_{\alpha\beta}^{\mathcal{D}}(r)$  (and  $C_{\alpha\beta}^{\mathcal{D}}(r)$ ) in equation (39), it can be shown that

$$\hat{h}_{\alpha\beta}^{\mathcal{D}}(r) = h_{\alpha\beta}^{\mathcal{D}}(r) - 3 \int_r^{\infty} dx h_{\alpha\beta}^{\mathcal{D}}(x)/x \quad (42)$$

$$\hat{c}_{\alpha\beta}^{\mathcal{D}}(r) = c_{\alpha\beta}^{\mathcal{D}}(r) - 3 \int_r^{\infty} dx c_{\alpha\beta}^{\mathcal{D}}(x)/x \quad (43)$$

Equations (42) and (43) are used directly to obtain the closure rules on the "hatted" functions appropriate for the coupled Ornstein-Zernike-like equations (40) and (41). The closure rules for the  $\Delta$ -coefficients remain unchanged (cf. equation (36)). Here,

$$\begin{aligned}\hat{h}_{\alpha\beta}^{\Delta}(r) &= 0 && \text{for } r < R_{\alpha\beta} \\ \hat{c}_{\alpha\beta}^{\Delta}(r) &= 0 && \text{for } r > R_{\alpha\beta}.\end{aligned}\quad (44)$$

Using  $h_{\alpha\beta}^D(r) = 0$  inside the hard core  $R_{\alpha\beta}$  and  $h_{\alpha\beta}^D(r) \neq 0$  elsewhere, the closure condition for  $\hat{h}_{\alpha\beta}^D(r)$  is

$$\begin{aligned}\hat{h}_{\alpha\beta}^D(r) &= -3 \int_{R_{\alpha\beta}}^{\infty} dx h_{\alpha\beta}^D(x)/x \quad \text{for } r < R_{\alpha\beta} \\ &= -3 K_{\alpha\beta}\end{aligned}\quad (45)$$

$$\hat{c}_{\alpha\beta}^D(r) = 0 \quad \text{for } r > R_{\alpha\beta}.$$

The vanishing of  $\hat{c}_{\alpha\beta}^D(r)$  outside the hard core is evident from substitution of the  $r^{-3}$  dependence (equation (37)) for  $|\vec{r}| > R_{\alpha\beta}$  into equation (43).

Thus, provided the anisotropic coupling terms in equations (40) and (41) can be removed, these equations can be solved in the same spirit as the Ornstein-Zernike equation has been solved for more conventional boundary conditions. Such a decoupling step is given from certain linear combinations of the "hatted" coefficients ( $\hat{h}_{\alpha\beta}^D(r)$ ,  $\hat{h}_{\alpha\beta}^{\Delta}(r)$ ,  $\hat{c}_{\alpha\beta}^D(r)$ , and  $\hat{c}_{\alpha\beta}^{\Delta}(r)$ ). As a consequence of nonequal radii, these linear combinations for mixtures do not reduce equations (40) and (41) to the simple Ornstein-Zernike equation

for hard spheres as found in the single component case. Nor is this reduction possible in the equal radii mixture problem given by Adelman and Deutch. It is found the most convenient linear combinations are

$$\begin{aligned} h_{\alpha\beta}^+(r) &= (\hat{h}_{\alpha\beta}^D(r) + \frac{1}{2}\hat{h}_{\alpha\beta}^A(r))/3 \\ h_{\alpha\beta}^-(r) &= (\hat{h}_{\alpha\beta}^D(r) - \hat{h}_{\alpha\beta}^A(r))/3, \end{aligned} \quad (46)$$

and

$$\begin{aligned} c_{\alpha\beta}^+(r) &= (\hat{c}_{\alpha\beta}^D(r) + \frac{1}{2}\hat{c}_{\alpha\beta}^A(r))/3 \\ c_{\alpha\beta}^-(r) &= (\hat{c}_{\alpha\beta}^D(r) - \hat{c}_{\alpha\beta}^A(r))/3. \end{aligned} \quad (47)$$

The  $\pm$  superscripts arise quite naturally in further Ornstein-Zernike-like equations, this time for  $h_{\alpha\beta}^{\pm}(r)$  and  $c_{\alpha\beta}^{\pm}(r)$ . Explicitly the new closure relations are hard sphere-like,

$$\begin{aligned} h_{\alpha\beta}^{\pm}(r) &= -K_{\alpha\beta} & \text{for } |\vec{r}| < R_{\alpha\beta} \\ c_{\alpha\beta}^{\pm}(r) &= 0 & \text{for } |\vec{r}| > R_{\alpha\beta}, \end{aligned} \quad (48)$$

since the  $K_{\alpha\beta}$  are constants dependent on the independent variables density, mole fraction and temperature and molecular parameters diameters and dipole moments. Equations (48) follow immediately from the definitions (46) and (47) and the previous closure relations for the hatted functions, equations (44) and (45).

Using equations (46) and (47) in equations (40) and (41), the decoupling of the original Ornstein-Zernike equation is complete, and is given by equation (34) and the following pair (for details, see Appendix 5):

$$h_{\alpha\beta}^+(r_{12}) = c_{\alpha\beta}^+(r_{12}) + \sum_{\gamma} 2\rho_{\gamma} \int d\vec{r}_3 h_{\alpha\gamma}^+(r_{13}) c_{\gamma\beta}^+(r_{32}) \quad (49)$$

$$h_{\alpha\beta}^-(r_{12}) = c_{\alpha\beta}^-(r_{12}) + \sum_{\gamma} -\rho_{\gamma} \int d\vec{r}_3 h_{\alpha\gamma}^-(r_{13}) c_{\gamma\beta}^-(r_{32}). \quad (50)$$

Equations (34), (49) and (50) will be solved in the next Section using Baxter's factorized Ornstein-Zernike equation. At this point it is important to summarize the determination of the actual radial coefficients (cf. equations (16) and (17)) from the solutions of equations (49) and (50). Particular emphasis will be given to the anisotropic direct correlation functions, but corresponding equations are obvious for  $h_{\alpha\beta}^D(r)$  and  $h_{\alpha\beta}^A(r)$ .

From equation (47), hatted correlation functions can be written in terms of known functions (as in equations (49) and (50))  $c_{\alpha\beta}^{\pm}(r)$  as

$$\hat{c}_{\alpha\beta}^A(r) = 2 (c_{\alpha\beta}^+(r) - c_{\alpha\beta}^-(r))$$

$$\hat{c}_{\alpha\beta}^D(r) = 2 (c_{\alpha\beta}^+(r) + \frac{1}{2} c_{\alpha\beta}^-(r)) \quad (51)$$

In order to benefit from knowledge of  $c_{\alpha\beta}^D(r)$ , it is necessary to invert equation (33) for  $c_{\alpha\beta}^D(r)$  in terms of  $\hat{c}_{\alpha\beta}^D(r)$ . The first step here is to rewrite equation (25) in terms

of the Laplacian operator

$$C_{\alpha\beta}^D(r) = \nabla^2 C_{\alpha\beta}^D(r) - \frac{3}{r} \frac{dC_{\alpha\beta}^D(r)}{dr} . \quad (52)$$

Since  $r^2 \nabla^2 f(r) = \frac{d}{dr} (r^2 \frac{df}{dr})$  can be integrated to give an expression for the first derivative of any function in terms of the Laplacian of that function, it follows

$$\frac{dC_{\alpha\beta}^D(r)}{dr} = \frac{1}{r} \int dx x^2 \hat{C}_{\alpha\beta}^D(x) + \text{constant} .$$

From equation (26) this derivative behaves as  $r K_{\alpha\beta}$  for  $r \rightarrow 0$  and so the constant of integration is zero for the definite integral  $0 < x < r$ . Thus equation (52) becomes

$$C_{\alpha\beta}^D(r) = \hat{C}_{\alpha\beta}^D(r) - 3r^{-3} \int_0^r dx x^2 \hat{C}_{\alpha\beta}^D(x) . \quad (53)$$

A similar equation can be written down for  $h_{\alpha\beta}^D(r)$ .

Although equation (53) holds for all  $r$ , it can be used in a self-consistent approach to calculate the fundamental, yet undetermined,  $K_{\alpha\beta}$ . Restricting  $|\vec{r}| > R_{\alpha\beta}$ , the closure relation on  $\hat{C}_{\alpha\beta}^D(r)$  gives zero contribution to the first term and also places an upper limit  $r = R_{\alpha\beta}$  in the remaining term. So for  $|\vec{r}| > R_{\alpha\beta}$  the right hand side of equation (53) becomes

$$C_{\alpha\beta}^D(r) = -3r^{-3} \int_0^{R_{\alpha\beta}} dx x^2 \hat{C}_{\alpha\beta}^D(x) .$$

Yet the Mean Spherical Approximation ensures in this domain,

$|\vec{r}| > R_{\alpha\beta}$ , that  $c_{\alpha\beta}^D(r) = m_{\alpha} m_{\beta} / (kT r^3)$  (from equation (37)) on

the left hand side. Cancelling the common  $r^{-3}$  factor, the self-consistency condition for the  $K_{\alpha\beta}$  is

$$\frac{m_{\alpha} m_{\beta}}{3KT} = - \int_0^{R_{\alpha\beta}} dx \, x^2 \hat{c}_{\alpha\beta}^D(x) . \quad (54)$$

The right hand side is identified as the density derivative of the chemical potential of species  $\alpha$  with respect to species  $\beta$  if a factor of  $4\pi\sqrt{\rho_{\alpha}\rho_{\beta}}$  were present (Lebowitz and Rowlinson, 1964). Multiplying both sides by  $4\pi\sqrt{\rho_{\alpha}\rho_{\beta}}$  and substituting for  $\hat{c}_{\alpha\beta}^D(r)$  from equation (51) gives

$$\frac{4\pi m_{\alpha} m_{\beta} \sqrt{\rho_{\alpha}\rho_{\beta}}}{3KT} = -\sqrt{\rho_{\alpha}\rho_{\beta}} \int d\vec{r} \, (2c_{\alpha\beta}^+(r) + c_{\alpha\beta}^-(r)) . \quad (55)$$

For a two-component mixture this condition is really a set of three nonlinear algebraic equations for  $K_{11}$ ,  $K_{22}$  and  $K_{12} = K_{21}$ . Since this thesis is concerned in the thermodynamic properties of binary mixtures of polar molecules, higher order component systems will not be considered. However it must be mentioned that up to this point all equations are valid for a general  $n$ -component system.

Thermodynamically, the numerical solution of equation (55) for the  $K_{\alpha\beta}$ 's is dependent on evaluation of the right hand side, i.e., solving the Ornstein-Zernike equation for the "hard sphere-like" boundary conditions of equation (48). This will be done in the following sections using Baxter's method originally developed for mixtures of hard spheres. Both boundary conditions will be examined.

#### 4. The Equations for Hard Sphere Mixtures

The spherically symmetric term of the direct and indirect correlation functions for dipolar hard sphere mixtures requires the solution of the Ornstein-Zernike equation for mixtures of hard spheres. Also from the previous Section, the behaviour of the anisotropic terms are intimately connected with solution of a corresponding problem for certain pseudo-hard sphere mixtures. Both cases can be solved using Baxter's factorized form of the Ornstein-Zernike equation.

Before the advent of Baxter's factorization method, analytic solutions had only been obtained for the hard sphere potential for single and multicomponent fluids in the Percus-Yevick approximation. Wertheim (1963) and Lebowitz (1964) essentially factorized the Laplace transform of the Ornstein-Zernike equation for the single and multicomponent case respectively. Both methods were specific for a description of the hard sphere potential within the Percus-Yevick closure relation. However, Baxter (1968, 1970) has recently factorized the Ornstein-Zernike equation itself for single and multicomponent fluids independently of the type of closure rules. In fact Baxter's elegant factorization can be used most efficiently for other liquid models provided the direct correlations are of finite range. The utility of Baxter's transformation cannot be overstressed. The end result is two coupled integral equations which present analytic expressions for the inverse compressibility and the compressibility pressure of hard spheres. For nontrivial fluid models the linearity of these equations in the direct and indirect correlation functions ensure fast convergence when using numerical methods.

For any mixture, in which the  $\alpha$  -component has a range parameter  $R_\alpha$  and number density  $\rho_\alpha$ , the Ornstein-Zernike equation is

$$h_{\alpha\beta}(r_{12}) = c_{\alpha\beta}(r_{12}) + \sum_{\gamma} \rho_{\gamma} \int d\vec{r}_3 c_{\alpha\gamma}(r_{13}) h_{\gamma\beta}(r_{32}). \quad (56)$$

Baxter's transformation (a Wiener-Hopf factorization (Noble, 1958) to use more explicit terms) gives

$$r c_{\alpha\beta}(r) = -q'_{\alpha\beta}(r) + 2\pi \sum_{\gamma} \rho_{\gamma} \int_{S_{\gamma\alpha}}^{\min(R_{\gamma\alpha}, R_{\gamma\beta}-r)} dt q_{\gamma\alpha}(t) q'_{\gamma\beta}(r+t) \quad (57)$$

$$r h_{\alpha\beta}(r) = -q'_{\alpha\beta}(r) + 2\pi \sum_{\gamma} \rho_{\gamma} \int_{S_{\alpha\gamma}}^{R_{\alpha\gamma}} dt q_{\alpha\gamma}(t) (r-t) h_{\gamma\beta}(r-t) \quad (58)$$

and

$$q_{\alpha\beta}(R_{\alpha\beta}) = 0$$

where  $q'_{\alpha\beta}(r)$  is the derivative of  $q_{\alpha\beta}(r)$  with respect to  $r$ .

Equations (57) and (58) are derived from equation (56) under the assumptions that (a) the fluid is disordered so that  $\int dr r h(r)$  exists and is bounded, (b) the direct correlation function vanishes outside the associated range parameters  $R_{\alpha\beta}$ , i.e.,  $c_{\alpha\beta}(r) = 0$  for  $r > R_{\alpha\beta}$ . The associated range parameters  $R_{\alpha\beta}$  and  $S_{\alpha\beta}$  are simply

$$R_{\alpha\beta} = (R_\alpha + R_\beta)/2 \quad (59)$$

$$S_{\alpha\beta} = (R_\alpha - R_\beta)/2. \quad (60)$$

Equations (57) and (58) are to be solved when  $r$  is restricted to the domains  $S_{\alpha\beta} < r < R_{\alpha\beta}$  and  $r > S_{\alpha\beta}$ , respectively. These equations are further supplemented by any closure relation desired. Baxter's solution to the Percus-Yevick approximation of hard sphere mixtures will be summarized here since further use will be made of the method in the next Section.

A mixture of hard spheres of additive diameters  $\{R_{\alpha}\}$  and number densities  $\{\rho_{\alpha}\}$  is treated in the Percus-Yevick approximation (equivalently the Mean Spherical Approximation) by the closure relations

$$h_{\alpha\beta}(r) = -1 \quad \text{for} \quad r < R_{\alpha\beta} \quad (61)$$

and

$$c_{\alpha\beta}(r) = 0 \quad \text{for} \quad r > R_{\alpha\beta} . \quad (62)$$

Here the same notation is used for the range parameters and associated quantities, and the additive diameters  $R_{\alpha\beta}$ . The equivalence is given by the Percus-Yevick approximation for hard spheres. Solving equations (57), (58) using the definitions (59), (60) under the restrictions imposed by equations (61) and (62) gives the solution for the Percus-Yevick approximation for hard sphere mixtures.

To this end, restricting  $S_{\alpha\beta} < r < R_{\alpha\beta}$  in equation (58) and substituting of  $h_{\alpha\beta}(r) = -1$  (being consistent with the values of  $r$  and  $t$ ) gives

$$g'_{\alpha\beta}(r) = a_{\alpha} r + b_{\alpha} . \quad (63)$$

The coefficients  $a_\alpha$  and  $b_\alpha$  are to be determined from

$$a_\alpha = 1 - 2\pi \sum_\gamma \rho_\gamma \int_{S_{\alpha\gamma}}^{R_{\alpha\gamma}} dt g_{\alpha\gamma}(t) \quad (64)$$

and

$$b_\alpha = 2\pi \sum_\gamma \rho_\gamma \int_{S_{\alpha\gamma}}^{R_{\alpha\gamma}} dt t g_{\alpha\gamma}(t). \quad (65)$$

Integration of equation (63) and use of  $q_{\alpha\beta}(R_{\alpha\beta}) = 0$  gives

$$g_{\alpha\beta}(r) = \frac{1}{2} a_\alpha (r^2 - R_{\alpha\beta}^2) + b_\alpha (r - R_{\alpha\beta}). \quad (66)$$

Subsequent evaluation of the integrals involved in equations (64) and (65) gives a set of linear equations in  $a_\alpha$  and  $b_\alpha$  with known constant coefficients.

If it were desired to obtain  $c_{\alpha\beta}(r)$  explicitly, this could now be done easily from equation (57). However the thermodynamic properties of a mixture of hard spheres can be determined from certain integrals involving  $c_{\alpha\beta}(r)$ . For example, the  $\beta$ -species density derivative of the chemical potential of species  $\alpha$  and the  $\beta$ -species density derivative of the pressure are given in terms of the integral,  $\int d\vec{r} c_{\alpha\beta}(r)$ . Explicitly, (Lebowitz and Rowlinson, 1964),

$$\frac{1}{kT} \frac{\partial \mu_\alpha}{\partial \rho_\beta} = \frac{\delta_{\alpha\beta}}{\rho_\alpha} - \int d\vec{r} c_{\alpha\beta}(r)$$

and

$$\frac{1}{kT} \frac{\partial p}{\partial \rho_\beta} = 1 - \sum_\alpha \rho_\alpha \int d\vec{r} c_{\alpha\beta}(r).$$

The integral  $\int d\vec{r} c_{\alpha\beta}(r)$  can be interpreted as the Fourier transform of  $c_{\alpha\beta}(r)$  evaluated at  $k = 0$ . With such an approach, it is possible to evaluate this limiting form of the Fourier transform in terms of the transform of  $q_{\alpha\beta}(r)$ . In obtaining the thermodynamic quantities through  $\int d\vec{r} c_{\alpha\beta}(r)$ , the following treatment explicitly sets out the factorization of the Ornstein-Zernike equation in terms of the associated Fourier transforms of the  $h_{\alpha\beta}$ ,  $c_{\alpha\beta}$  and  $q_{\alpha\beta}$  functions.

The factorization can be written down in terms of the Fourier transform of  $q_{\alpha\beta}(r)$ ,  $\tilde{q}_{\alpha\beta}(K)$ , defined by

$$\tilde{q}_{\alpha\beta}(K) = \delta_{\alpha\beta} - 2\pi\sqrt{\rho_\alpha\rho_\beta} \int_{S_{\alpha\beta}}^{R_{\alpha\beta}} dr e^{iKr} q_{\alpha\beta}(r). \quad (67)$$

The factorization is explicitly given in

$$\begin{aligned} \delta_{\alpha\beta} - \sqrt{\rho_\alpha\rho_\beta} \int d\vec{r} e^{i\vec{K}\cdot\vec{r}} c_{\alpha\beta}(r) \\ = \sum_{\gamma} \tilde{q}_{\gamma\alpha}(-K) \tilde{q}_{\gamma\beta}(K). \end{aligned}$$

Putting  $K = 0$  gives

$$\begin{aligned} \delta_{\alpha\beta} - 4\pi\sqrt{\rho_\alpha\rho_\beta} \int_0^{R_{\alpha\beta}} dr r^2 c_{\alpha\beta}(r) \\ = \delta_{\alpha\beta} - \tilde{C}_{\alpha\beta}(0) \\ = \sum_{\gamma} \tilde{q}_{\gamma\alpha}(0) \tilde{q}_{\gamma\beta}(0). \end{aligned} \quad (68)$$

Elementary calculus results in

$$\tilde{q}_{\alpha\beta}(0) = \delta_{\alpha\beta} + \frac{\pi}{6}\sqrt{\rho_\alpha\rho_\beta} R_\beta^2 (a_\alpha(3R_\alpha + R_\beta) + 6b_\alpha), \quad (69)$$

and using equation (69) in (68)

$$\begin{aligned}
 -\tilde{C}_{\alpha\beta}(0) = & \frac{\pi}{6} \sqrt{\rho_{\alpha}\rho_{\beta}} \left[ \frac{(R_{\alpha}+R_{\beta})^3}{(1-\xi_3)} \right. \\
 & + \frac{3R_{\alpha}R_{\beta}\xi_2(R_{\alpha}^2+R_{\beta}^2) + 3R_{\alpha}^2R_{\beta}^2\xi_1(R_{\alpha}+R_{\beta}) + 9R_{\alpha}^2R_{\beta}^2\xi_2}{(1-\xi_3)^2} \\
 & + \frac{R_{\alpha}^3R_{\beta}^3\xi_0}{(1-\xi_3)^2} + \frac{9R_{\alpha}^2R_{\beta}^2\xi_2^2(R_{\alpha}+R_{\beta}) + 6R_{\alpha}^3R_{\beta}^3\xi_1\xi_2}{(1-\xi_3)^3} \\
 & \left. + \frac{9R_{\alpha}^3R_{\beta}^3\xi_2^3}{(1-\xi_3)^4} \right] \quad (70)
 \end{aligned}$$

Here  $\xi_K = \frac{\pi}{6} \sum_{\gamma} \rho_{\gamma} R_{\gamma}^K$  in keeping with Baxter's notation. Equation (70) may be integrated with respect to the total density keeping composition fixed to obtain the chemical potentials of each species. The results are in agreement with those of Lebowitz and Rowlinson (1964) and are presented here for completeness. In terms of de Broglie wavelength of species  $\alpha$ ,  $\Lambda_{\alpha} = h/(2\pi m_{\alpha}KT)^{\frac{1}{2}}$ , the chemical potential is

$$\begin{aligned}
 \beta\mu_{\alpha} = & \ln(\rho_{\alpha}\Lambda_{\alpha}^3) - \ln(1-\xi_3) + \frac{(R_{\alpha}^3\xi_0 + 3R_{\alpha}^2\xi_1 + 3R_{\alpha}\xi_2)}{(1-\xi_3)} \\
 & + \frac{(3R_{\alpha}^3\xi_1\xi_2 + \frac{9}{2}R_{\alpha}^2\xi_2^2)}{(1-\xi_3)^2} + \frac{3R_{\alpha}^3\xi_2^3}{(1-\xi_3)^3} \quad (71)
 \end{aligned}$$

The next Section shall utilize these techniques to obtain the solution of a closely associated problem.

## 5. Solution of the Ornstein-Zernike Equation for Pseudo-Hard Spheres

As already mentioned in Section 3, it is desired to obtain the integral  $\int dr C_{\alpha\beta}^{\pm}(r)$  for a system of pseudo-hard spheres. More specifically these pseudo-hard spheres are defined by the closure rules given in equation (48) (the  $\pm$  superscripts will be omitted in this Section and both cases are treated identically henceforth). Equations (49) and (50) are now to be solved under the restrictions of equation (48). The same procedure to obtain  $g_{\alpha\beta}(r)$  is repeated to give

$$g_{\alpha\beta}(r) = \frac{1}{2} a_{\alpha\beta} (r^2 - R_{\alpha\beta}^2) + b_{\alpha\beta} (r - R_{\alpha\beta}).$$

However, it should be noted the coefficients  $a_{\alpha\beta}$ ,  $b_{\alpha\beta}$  are no longer independent of  $\beta$  as in equations (63)-(65). This is explicitly seen in the following set of coupled linear equations:

$$a_{\alpha\beta} = 1 + \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_{\gamma}^{\alpha\beta} R_{\gamma}^2 \{ 3(a_{\alpha\gamma} R_{\alpha} + 2b_{\alpha\gamma}) + a_{\alpha\gamma} R_{\gamma} \}$$

(72)

and

$$b_{\alpha\beta} = -\frac{1}{2} \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_{\gamma}^{\alpha\beta} R_{\gamma}^2 \{ 3R_{\alpha} (a_{\alpha\gamma} R_{\alpha} + 2b_{\alpha\gamma}) - 2b_{\alpha\gamma} R_{\gamma} \}$$

(73)

where

$$\rho_{\gamma}^{\alpha\beta} = \rho_{\gamma} K_{\alpha\gamma} K_{\gamma\beta} / K_{\alpha\beta}.$$

It is easier to solve equations (72) and (73) for certain linear combinations of  $a_{\alpha\beta}$  and  $b_{\alpha\beta}$ . Those that will prove useful later in the analysis are

$$A_{\alpha\beta} = a_{\alpha\beta} R_{\alpha} + 2b_{\alpha\beta}$$

(74)

and

$$B_{\alpha\beta} = 3 A_{\alpha\beta} + a_{\alpha\beta} R_{\beta}. \quad (75)$$

Equations (74) and (75) are then transformed into

$$\begin{aligned} R_{\alpha} + \sum_{\gamma=1}^2 \left( \frac{\pi}{6} \rho_{\gamma}^{\alpha\beta} R_{\gamma}^3 - \delta_{\gamma\beta} \right) A_{\alpha\gamma} \\ = 0 \end{aligned} \quad (76)$$

and

$$\begin{aligned} \sum_{\gamma=1}^2 \left( \frac{\pi}{6} \rho_{\gamma}^{\alpha\beta} R_{\beta} R_{\gamma}^2 - \delta_{\gamma\beta} \right) B_{\alpha\gamma} \\ = 3 R_{\alpha} + R_{\beta} + 3 \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_{\gamma}^{\alpha\beta} R_{\gamma}^3 A_{\alpha\gamma}. \end{aligned} \quad (77)$$

It is simple to solve equation (76) for  $A_{\alpha\beta}$ , substitute into equation (77) (to evaluate the nonhomogeneous coupling term) and solve for  $B_{\alpha\beta}$ . This algebra is straight-forward and the details are given in Appendix 6. The results are

$$A_{\alpha\beta} = R_{\alpha} (1 + \xi_3^{\alpha\beta} - \xi_3^{12}) / D \quad (78)$$

and

$$\begin{aligned} B_{\alpha\beta} = & \frac{3R_{\alpha} + R_{\beta}}{D} + \frac{3R_{\alpha}R_{\beta}\xi_2^{\alpha\beta}}{D^2} \\ & + \frac{4R_{\alpha}(\xi_3^{\alpha\beta} - \xi_3^{12})}{D} \\ & - \frac{3\Delta(R_{\alpha} + R_{\beta})}{D^2} - \frac{3\Delta R_{\alpha}(\xi_3^{\alpha\beta} - \xi_3^{12})}{D^2} \end{aligned} \quad (79)$$

where

$$\xi_K^{\alpha\beta} = \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_{\gamma}^{\alpha\beta} R_{\gamma}^K$$

$$\Delta = \frac{\pi^2}{36} \rho_1^{12} R_1^3 \rho_2^{12} R_2^3 (1 - K_{12}^2 / (K_{11} K_{22}))$$

$$D = 1 - \xi_3^{12} + \Delta.$$

It should be noted that if  $K_{12}^2 = K_{11} K_{22}$ , then

$$A_{\alpha\beta} = R_{\alpha} / (1 - \xi_3^{12}) \quad (80)$$

and

$$B_{\alpha\beta} = \frac{3R_{\alpha} + R_{\beta}}{(1 - \xi_3^{12})} + \frac{3R_{\alpha}R_{\beta}\xi_2^{12}}{(1 - \xi_3^{12})^2} \quad (81)$$

with

$$\xi_K^{12} = \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_{\gamma} K_{\gamma\gamma} R_{\gamma}^K \quad (82)$$

On comparison with corresponding quantities in the previous Section, it is obvious that an equivalent hard sphere mixture with augmented densities  $\rho_1 K_{11}$  and  $\rho_2 K_{22}$  is obtained when  $K_{12}^2 = K_{11} K_{22}$ . However, it can be shown from the low density limit that this geometric mean condition is only valid for equal diameters,  $R_1 = R_2 = R$ . Then, in equations (80) - (82),  $A_{\alpha\beta}$  and  $B_{\alpha\beta}$  become species-independent and are determined by  $\rho_1 K_{11} + \rho_2 K_{22}$  and  $R$  only. In this way, the equal diameter mixture case reduces simply to an effective single component fluid. Any attempts to construct such effective densities in the hard sphere mixture equations for the nonequal diameter case fail. These give obvious inconsistencies for the densities in the Ornstein-Zernike equations for mixtures. In fact, these "effective densities",  $\rho_{\gamma}^{\alpha\beta} = K_{\alpha\gamma} K_{\gamma\beta} \rho_{\gamma} / K_{\alpha\beta}$  become species dependent and are ill-defined in the set of Ornstein-Zernike equations for mixtures. For example, the  $\alpha = \beta = 1$  equation would have the densities  $\rho_1 K_{11}$  and  $\rho_2 K_{12}^2 / K_{11}$ . These are inconsistent with the set of densities  $\rho_1 K_{12}^2 / K_{22}$ ,  $\rho_2 K_{22}$  and  $\rho_1 K_{11}$ ,  $\rho_2 K_{22}$  for the  $\alpha = \beta = 2$  and  $\alpha = 1, \beta = 2$  equations, res-

pectively. Therefore, an equivalent multicomponent hard sphere fluid at these augmented densities is not defined.

The analogue of equation (69) is

$$\tilde{q}_{\alpha\beta}(0) = \delta_{\alpha\beta} + \frac{\pi}{6} \sqrt{\rho_\alpha \rho_\beta} K_{\alpha\beta} R_\beta^2 B_{\alpha\beta}. \quad (83)$$

The desired integral  $\tilde{c}_{\alpha\beta}(0; \rho_1, \rho_2)$ , showing explicit density dependence, is given in terms of the  $B_{\alpha\beta}$  as

$$-\tilde{c}_{\alpha\beta}(0; \rho_1, \rho_2) = \frac{\pi}{6} \sqrt{\rho_\alpha \rho_\beta} K_{\alpha\beta} \left\{ R_\alpha^2 B_{\beta\alpha} + R_\beta^2 B_{\alpha\beta} + \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\alpha^2 B_{\gamma\alpha} R_\beta^2 B_{\gamma\beta} \right\}. \quad (84)$$

Equation (84) is now employed in the self-consistency equation (55). Reintroducing the  $\pm$  superscripts for the positive ( $2\rho$ ) and negative ( $-\rho$ ) densities, equation (55) becomes

$$\frac{4\pi m_\alpha m_\beta \sqrt{\rho_\alpha \rho_\beta}}{3KT} = -\tilde{c}_{\alpha\beta}^+(0; 2\rho_1, 2\rho_2) - \tilde{c}_{\alpha\beta}^-(0; -\rho_1, -\rho_2). \quad (85)$$

The set of equations (c.f. (85)) is to be solved for the  $K_{\alpha\beta}$ 's once the molecular system has been specified (i.e.,  $m_\alpha, \rho_\alpha$  given). For a two-component dipolar mixture these equations become

$$\frac{4\pi m_1^2 \rho_1}{3KT} = -\tilde{c}_{11}^+(0; 2\rho_1, 2\rho_2) - \tilde{c}_{11}^-(0; -\rho_1, -\rho_2),$$

$$\frac{4\pi m_2^2 \rho_2}{3KT} = -\tilde{c}_{22}^+(0; 2\rho_1, 2\rho_2) - \tilde{c}_{22}^-(0; -\rho_1, -\rho_2)$$

$$\frac{4\pi m_1 m_2 \sqrt{\rho_1 \rho_2}}{3KT} = -\tilde{c}_{12}^+(0; 2\rho_1, 2\rho_2) - \tilde{c}_{12}^-(0; -\rho_1, -\rho_2). \quad (86)$$

A fourth equation for  $\alpha = 2$ ,  $\beta = 1$  is identical to the  $\alpha = 1$ ,  $\beta = 2$  equation and is omitted.

#### 6. Special Limiting Cases

From equation (79) it can be shown that for low density and fixed composition

$$B_{\alpha\beta} = 3R_\alpha + R_\beta .$$

This limit allows the right hand side of equation (85) to be simplified, giving the low density behaviour of  $K_{\alpha\beta}$  as

$$K_{\alpha\beta} = \frac{m_\alpha m_\beta}{3KT R_{\alpha\beta}^3} . \quad (87)$$

The importance of the limiting behaviour of  $K_{\alpha\beta}$  is twofold. Firstly, it provides a starting point in any iteration scheme to solve equation (86) numerically. Furthermore, it shows the deviation from the geometric law  $K_{12}^2 = K_{11} K_{22}$  for non-equal diameters. Thus, the Ansatz of Adelman-Deutch (1973) is valid only for equal diameters, and due to the structure of equations (84) and (85) does not have any justification for non-equal diameters. In fact, the Ansatz holds for  $R_1 = R_2 = R_{12}$  because  $-\tilde{C}_{11}^{\dagger}$  and  $-\tilde{C}_{22}^{\dagger}$  are species independent and so simplify to the single-component result. For example, equation (84) becomes

$$-\tilde{C}_{\alpha\beta}(0; \rho_1, \rho_2) = \sqrt{\frac{\pi^2}{36} \rho_\alpha K_{\alpha\alpha} R_\alpha^3 \rho_\beta K_{\beta\beta} R_\beta^3} \times \frac{(4 - \xi_e)(2 + \xi_e^2)}{(1 - \xi_e)^4}$$

where

$$\xi_e = \frac{\pi}{6} (\rho_1 K_{11} + \rho_2 K_{22}) R^3 .$$

This allows the 1 - 1 and 2 - 2 equations to be added giving a single component-like result

$$\begin{aligned} \frac{4\pi(m_1^2\rho_1+m_2^2\rho_2)}{3KT} \\ = Q(2\xi_e) - Q(-\xi_e) \end{aligned} \quad (88)$$

where the compressibility  $Q(\xi)$  is given in

$$\begin{aligned} Q(\xi) &= 1 + \frac{\xi(4-\xi)(2+\xi^2)}{(1-\xi)^4} \\ &= \frac{(1+2\xi)^2}{(1-\xi)^4} . \end{aligned}$$

The 1 - 2 equation in the equal radii case is merely redundant, as it satisfies the identity  $(11) \times (22) = (12)^2$  . Such simplification is again not possible in the more general case considered here. Even a reduction to the calculation of Percus-Yevick hard sphere mixture properties is prohibited through the inconsistent definitions of the associated densities.

### Chapter 3

#### The Calculation of Thermodynamic Properties of a Mixture of Dipolar Hard Spheres

##### 1. Introduction

In this Chapter, the solution of the Mean Spherical Approximation for dipolar mixtures will be used to examine phase transitions at the molecular level. It is well-known (Prigogine and Defay, 1973; Rowlinson, 1971) that phase transitions in mixtures are described by the occurrence of instabilities (with respect to phase separation) in any single phase system. Furthermore, such instabilities are mathematically determined by finding regions of (pressure, temperature, composition) space where the second derivative of the Gibbs free energy of the mixture with respect to composition is negative. Such a search procedure is usually done by finding the concave-downward behaviour in a composition plot of the Gibbs free energy of the mixture given a constant pressure and a constant temperature. The actual limits of the composition range over which the one phase system splits into two phases (i.e. mixing does not take place) are given in the common tangent construction. Using well-known thermodynamic arguments (Rowlinson, 1971), it can be shown that the geometry of the common tangent construction yields the compositions of phases which are indeed at equilibrium as measured by equality of temperature, pressure and chemical potentials.

If the components of the mixture are miscible in all proportions at a given temperature and a given pressure, the behaviour described above disappears. Here the composition graph of the Gibbs free energy of the mixture is concave-upwards, i.e.,

the second derivative of the Gibbs free energy of the mixture with respect to composition (with pressure and temperature held constant) is positive over all compositions. The change in behaviour from immiscibility to miscibility at constant pressure defines the critical solution temperature. In fact, the critical lines of  $p$ ,  $T$ ,  $x$ -phase diagrams are the collection of the pressure dependence of the critical solution temperatures and critical compositions of the various types of phase changes.

Thus, any molecular interpretation of such phase diagrams is based on knowledge of the Gibbs free energy as a function of pressure, temperature and composition. In our case these details are provided by the statistical thermodynamical properties calculated for dipolar mixtures in the Mean Spherical Approximation. In Section 2, the Gibbs free energy for a dipolar mixture is given as a function of the volume, temperature and composition according to standard statistical thermodynamic equations. The replacement of the volume by the pressure as the independent variable in the Gibbs free energy of the mixture is necessitated by the material stability criterion and is carried out in Section 3. The above steps in calculating the Gibbs free energy as a function of pressure, temperature and composition require extensive numerical calculations on a computer. Section 4 contains the relevant numerical details and techniques involved in the calculation. Finally, the analysis of the composition plot of the Gibbs free energy of the mixture is given in Section 5. Here, the common tangent construction details the compositions of those phases in equilibrium.

## 2. Statistical Mechanical Formulae

The Helmholtz free energy for a dipolar hard sphere mixture can be written as

$$A = A_0(N_1, N_2, V, T) + \Delta A(N_1, N_2, V, T) \quad , \quad (1)$$

where  $A_0$  is the Helmholtz free energy of a mixture of hard spheres and  $\Delta A$  is the dipolar contribution to the Helmholtz free energy.

The variables  $N_1, N_2, V, T$  are the number of dipolar hard spheres of species one and two, the volume and the absolute temperature, respectively. In this thesis,  $A_0$  will be given by the Mansoori-Carnahan-Starling-Leland (1971) free energy derived from their empirical equation of state for a mixture of hard spheres.  $\Delta A$  is calculated according to the statistical thermodynamical properties obtained from the solution of the Mean Spherical Approximation of dipolar mixtures. Equation (1) implies that the pressure

$P = -(\partial A / \partial V)_{N_1, N_2, T}$  can be written as the sum of a hard sphere term  $p_0$  plus a dipolar term  $\Delta p$  which is in excess of the hard sphere contribution. Then

$$P = p_0(N_1, N_2, V, T) + \Delta p(N_1, N_2, V, T) \quad . \quad (2)$$

The Gibbs free energy can be similarly decomposed into a hard sphere reference term and a dipolar contribution. In fact this decomposition of  $G = A + pV$  follows immediately from equations (1) and (2) as

$$G = G_0(N_1, N_2, V, T) + \Delta G(N_1, N_2, V, T) \quad , \quad (3)$$

where

$$G_0 = A_0(N_1, N_2, V, T) + p_0(N_1, N_2, V, T) V \quad (4)$$

and

$$\Delta G = \Delta A(N_1, N_2, V, T) + \Delta p(N_1, N_2, V, T) V \quad . \quad (5)$$

In equations (1) and (3)-(5), it should be noted that the volume  $V$  is used as an independent variable rather than the pressure  $p$ . This is a consequence of the solution of the Mean Spherical Approximation and thermodynamic properties being given in terms of the canonical  $(N_1, N_2, V, T)$  ensemble. The pressure dependence of the thermodynamic properties is implicitly given through the equation of state for the mixture, equation (2) above. The thermodynamics of the hard sphere reference state and the corresponding excess quantities due to dipolar interactions will be detailed in the subsections below.

## 2.1 Properties of the Hard Sphere Reference State

The basis of the calculation for the contribution of the hard sphere mixture to any thermodynamic property described above is the equation of state for a mixture of hard spheres. Mansoori et al., (1971) have proposed a semiempirical equation of state for hard sphere mixtures. This simple equation of state gives excellent results for the corresponding thermodynamic properties on comparison with machine simulation results. These features of simplicity and accuracy make the Mansoori-Carnahan-Starling-Leland equation of state an ideal choice as a reference state to describe properties of the hard sphere mixture. It should be remembered that the

$N_1, N_2, V$  and  $T$  are the same for the hard sphere and dipolar hard sphere mixtures. Then the dipolar contribution is definitely in excess of the properties of the hard sphere mixture of the same number of different molecules and same volume.

In the approach of Mansoori et al., the pressure is written as a weighted average of the Percus-Yevick compressibility pressure  $p^c$  and virial pressure  $p^v$ , the respective weights being  $2/3$  and  $1/3$ . Such a scheme has some justification for the single component case of hard sphere fluids studied earlier by Carnahan and Starling (1969) and the mixture results are a straightforward extension of the highly successful Carnahan-Starling equation of state to mixtures of hard spheres. Now, Baxter (1970) has solved the Percus-Yevick equation for mixtures of hard spheres in a form different from that used by Mansoori et al. In his notation,  $p^c$  is written in terms of  $\xi_K = \frac{\pi}{6} \sum_{\gamma=1}^2 \rho_{\gamma} R_{\gamma}^K$  as

$$\frac{p^c}{KT} = \frac{6}{\pi} \left\{ \frac{\xi_0}{(1-\xi_3)} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{3\xi_2^3}{(1-\xi_3)^3} \right\}. \quad (6)$$

The virial term is directly related to Baxter's  $p^c$  by the Rowlinson-Lebowitz (1964) result that

$$\frac{p^v}{KT} = \frac{p^c}{KT} - \frac{18}{\pi} \frac{\xi_3 \xi_2^3}{(1-\xi_3)^3}. \quad (7)$$

Using equations (6) and (7) in

$$\frac{p_0}{KT} = \frac{1}{3} \frac{p^v}{KT} + \frac{2}{3} \frac{p^c}{KT},$$

it is easy to write down the formula of Mansoori et al. as

$$\frac{p_0}{KT} = \frac{6}{\pi} \left\{ \frac{\xi_0}{(1-\xi_3)} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{\xi_2^3(3-\xi_3)}{(1-\xi_3)^3} \right\}. \quad (8)$$

Equation (8) is more aesthetically pleasing and easier to integrate than the original formula of Mansoori et al. The Helmholtz free energy corresponding to the pressure given in equation (8) is obtained from the volume integration of  $dA_0 = -p_0 dV$  at fixed temperature and numbers of molecules. For any arbitrary volume  $V_0$ ,

$$A_0(N_1, N_2, V, T) = A(N_1, N_2, V_0, T) - \int_{V_0}^V dV p_0(N_1, N_2, V, T).$$

As  $V_0 \rightarrow \infty$ ,  $A(N_1, N_2, V_0, T)$  describes the free energy of an ideal gas mixture which has a logarithmic divergence in  $V_0$ . Such singular behaviour also occurs in the Helmholtz free energy of an ideal gas mixture under the same conditions, i.e.,

$$A^{id}(N_1, N_2, V, T) = \lim_{V_0 \rightarrow \infty} A^{id}(N_1, N_2, V_0, T) - \lim_{V_0 \rightarrow \infty} \int_{V_0}^V dV p^{id}(N_1, N_2, V, T).$$

Subtracting this ideal behaviour term from the hard sphere mixture expression gives an expression which is free of this singular behaviour,

$$A_0(N_1, N_2, V, T) = A^{id}(N_1, N_2, V, T) - \lim_{V_0 \rightarrow \infty} \int_{V_0}^V dV (p_0(N_1, N_2, V, T) - p^{id}(N_1, N_2, V, T))$$

Replacing the volume variable by the total number density  $\rho$  where

$V = N/\rho$ ,  $N = N_1 + N_2$ , the Helmholtz free energy of a mixture of hard spheres in excess of a mixture of ideal gases at the same  $N_1, N_2, V$  and  $T$  is

$$\frac{A_0(N_1, N_2, V, T) - A^{id}(N_1, N_2, V, T)}{NKT}$$

$$= \lim_{\rho_0 \rightarrow 0} \int_{\rho_0}^{\rho} d\rho \rho^{-1} \left( \frac{p_0}{\rho KT} - 1 \right). \quad (9)$$

Using equation (8) for  $p_0/KT$  in the integrand above, it is straightforward to show

$$\begin{aligned} \frac{A_0(N_1, N_2, V, T) - A^{id}(N_1, N_2, V, T)}{NKT} \\ = \left( \frac{\xi_2^3}{\xi_0 \xi_3^2} - 1 \right) \ln(1 - \xi_3) + \frac{3 \xi_1 \xi_2}{\xi_0 (1 - \xi_3)} \\ + \frac{\xi_2^3}{\xi_3 \xi_0 (1 - \xi_3)^2} . \end{aligned} \quad (10)$$

The determination of the Gibbs free energy follows from the use of equations (8) and (10) for  $p_0$  and  $A_0$  in equation (4). In terms of the Gibbs free energy of a mixture of ideal gases,  $G_{mixt}^{id}(N_1, N_2, V, T)$ , the Gibbs free energy is given as

$$\begin{aligned} G_0(N_1, N_2, V, T) = G_{mixt}^{id}(N_1, N_2, V, T) + p_0 V - NKT \\ + NKT \left\{ \left[ \frac{\xi_2^3}{\xi_0 \xi_3^2} - 1 \right] \ln(1 - \xi_3) \right. \\ \left. + \frac{3 \xi_1 \xi_2}{\xi_0 (1 - \xi_3)} + \frac{\xi_2^3}{\xi_3 \xi_0 (1 - \xi_3)^2} \right\} . \end{aligned} \quad (11)$$

In equation (11),

$$G_{mixt}^{id}(N_1, N_2, V, T) = \sum_{\alpha=1}^2 N_{\alpha} KT \left[ \ln \Lambda_{\alpha}^3 + \ln(N_{\alpha}/V) \right] \quad (12)$$

where  $\Lambda_{\alpha} = h / (2\pi m_{\alpha} KT)^{\frac{1}{2}}$  is the thermal de Broglie wavelength for molecules of species  $\alpha$  with mass  $m_{\alpha}$ . A relationship giving the corresponding quantity  $G_{mixt}^{id}(N_1, N_2, p_0, T)$  of equation (12) is

$$G_{mixt}^{id}(N_1, N_2, V, T) = G_{mixt}^{id}(N_1, N_2, p_0, T) - NKT \ln Z_0 \quad (13)$$

where  $Z_0$  is the compressibility factor,  $Z_0 = p_0 V / N K T$ .

The above equations give the excess Gibbs free energy of a mixture of hard spheres over the ideal gas mixture at the same pressure and temperature. That is

$$\begin{aligned}
 G_o^{\text{ex}}(N_1, N_2, p, T) &= G_o(N_1, N_2, p, T) - G_{\text{mixt}}^{\text{id}}(N_1, N_2, p, T) \\
 &= pV - NKT - NKT \ln Z \\
 &\quad + NKT \left\{ \left[ \frac{\xi_2^3}{\xi_0 \xi_3} - 1 \right] \ln(1 - \xi_3) \right. \\
 &\quad \left. + \frac{3 \xi_1 \xi_2}{\xi_0 (1 - \xi_3)} + \frac{\xi_2^3}{\xi_0 (1 - \xi_3)^2} \right\}. \quad (14)
 \end{aligned}$$

Mansoori et al. have shown that equation (14) gives excess properties of hard sphere mixtures in excellent agreement with the molecular dynamics data of Alder. Here,  $p$  is the hard sphere mixture,  $p_0$  given by equation (4). Thus, the thermodynamic properties of a mixture of hard spheres are accurately determined from the equation of state of Mansoori et al. This approach will be used to calculate the hard sphere contribution to the thermodynamic properties of mixtures of dipolar hard spheres. In particular, equation (11) gives the hard sphere contribution to the Gibbs free energy of a dipolar hard sphere system considered at the same volume and temperature. The pressure dependence of this contribution can be determined in the same manner as those steps above leading to equation (14). Here, the pressure referred to is that of the mixture of dipolar hard spheres, not that of the hard sphere species as taken before. The following Section deals with those dipolar quantities which are in excess of the hard sphere contributions calculated above.

## 2.2 Properties of the Dipolar Hard Sphere Mixture

In this Section, contributions to the pressure and Helmholtz free energy which arise from dipolar interactions will be given. Such properties of a mixture of dipolar hard spheres are most conveniently calculated as an excess over the corresponding properties of a mixture of hard spheres with the same number of the various sized hard cores, which are considered at the same temperature and volume. Obviously, this choice of independent variables  $N_1, N_2, V$  and  $T$  is a direct consequence of the conditions of the Mean Spherical Approximation having been stated in terms of those variables appropriate to the canonical ensemble. Such dependence should be written explicitly, e.g.,  $K_{\alpha\beta} = K_{\alpha\beta}(N_1, N_2, V, T; m_1, m_2, R_1, R_2)$ . However, such notation is lengthy and cumbersome, and so is suppressed.

The method of calculation of the excess thermodynamic properties is based on the well-known charging process of statistical thermodynamics (Hill, 1956). For example, the excess Helmholtz free energy can be calculated as an integral over the internal energy which is associated with such a charging process. Actually, the associated charging parameter usually employed in such a scheme would give the relative amount of dipole moment as  $\sqrt{\lambda} m_\alpha$  where  $0 \leq \lambda \leq 1$ . Here the  $\lambda = 0$  state corresponds to a system of hard spheres, while the  $\lambda = 1$  state would give the dipolar hard sphere system, with dipole moments  $m_\alpha$ . However such a charging process is equivalent to an integration over the inverse temperature  $\beta$ . This will be used here numerically to find the excess Helmholtz free energy of a mixture of dipolar hard spheres from the  $\beta$  integration of the dipolar contribution to the internal

energy of the mixture. From equation (26) of Chapter 1, the dipolar contribution to the internal energy is

$$\Delta E = -\frac{4\pi}{3} V \sum_{\alpha \beta} \rho_{\alpha} \rho_{\beta} m_{\alpha} m_{\beta} K_{\alpha \beta} . \quad (15)$$

Given  $\Delta E$  in equation (15), the dipolar part of the Helmholtz free energy is then given by the integration of  $\beta d(\Delta A) = \Delta E(\beta) d\beta$  as

$$\begin{aligned} \Delta A &= \beta^{-1} \int_0^{\beta} d\beta' \Delta E(\beta') \\ &= -\frac{4\pi V}{3\beta} \sum_{\alpha \beta} \rho_{\alpha} \rho_{\beta} m_{\alpha} m_{\beta} \int_0^{\beta} d\beta' K_{\alpha \beta}(\beta'). \end{aligned} \quad (16)$$

Here the integral is evaluated at constant  $\rho_{\alpha}$ . The more familiar charging process is given by the change of variables  $\lambda = \beta' / \beta$ ,  $d\lambda = d\beta' / \beta$ . Then equation (16) becomes

$$\Delta A = -\frac{4\pi V}{3} \sum_{\alpha \beta} \rho_{\alpha} \rho_{\beta} m_{\alpha} m_{\beta} \int_0^1 d\lambda K_{\alpha \beta}(\lambda). \quad (17)$$

Equations (16) and (17) give the equivalent formulations of the Helmholtz free energy in terms of a temperature integration and a charging process. It should be pointed out that it is possible to carry out the integration analytically for the pure fluid.

Rushbrooke et al. found a closed form expression for the Helmholtz free energy from the formal expression of Nienhuis and Deutch (the pure component version of equation (16)) after an integration by parts. However for the mixture case the integration in equation (16) will be done numerically.

The dipolar contribution to the pressure is given by the difference in equations (15) and (16).

$$\Delta p = \frac{\Delta E}{V} - \frac{\Delta A}{V} \quad (18)$$

$$= -\frac{4\pi}{3} \sum_{\alpha\beta} \rho_{\alpha} \rho_{\beta} m_{\alpha} m_{\beta} \left( K_{\alpha\beta} - \beta^{-1} \int_0^{\beta} d\beta' K_{\alpha\beta}(\beta') \right). \quad (19)$$

Equation (18) follows from the general property of the Mean Spherical Approximation that the thermodynamic functions are determined from the product of volume and temperature. For mixtures of dipolar hard spheres, this dependence is given by the  $\sqrt{\rho_{\alpha}\rho_{\beta}} K_{\alpha\beta}$  in equation (79) being determined by  $\rho_1 \beta m_1^2$  and  $\rho_2 \beta m_2^2$ . Equations (5) and (17) also give the identity between the dipolar contributions to the internal energy and the Gibbs free energy

$$\begin{aligned} \Delta G &= \Delta E \\ &= -\frac{4\pi}{3} V \sum_{\alpha\beta} \rho_{\alpha} \rho_{\beta} m_{\alpha} m_{\beta} K_{\alpha\beta}. \end{aligned} \quad (20)$$

The following Section details the calculation of the pressure dependence of  $G_0 + \Delta G$ , as is required in the composition plot of the Gibbs free energy of the mixture at constant temperature and pressure.

### 3. $G = G(p, T, x)$

The stability criteria and coexistence construction for mixtures require the Gibbs free energy of the mixture as a function of pressure, temperature and composition. Unfortunately, the statistical mechanical calculation of the Gibbs free energy of the mixture depends on the independent variables volume, temperature and composition. This is explicitly shown in equations (3), (10), (11) and (20) above, where the arguments of the Gibbs free energy are  $N_1, N_2, V$  and  $T$ . The replacement of the volume by the pressure as the independent variable in such expressions is therefore an important step and will be described in this Section.

Firstly, such a substitution cannot be done directly since the Mean Spherical Approximation is formulated in terms of the Ornstein-Zernike equation which in turn is dependent on the number densities (i.e. the volume) rather than the pressure variable. In order to use the solution of the Mean Spherical Approximation to describe the dipolar contributions to the thermodynamic properties of dipolar hard sphere mixtures, it is then necessary to use the following indirect procedure. The arguments in the Gibbs free energy  $N_1, N_2, V$  and  $T$  also determine the pressure  $p = p(N_1, N_2, V, T)$  according to equations (2), (8), and (18). Such an equation can be inverted (at least formally) to obtain the volume as a function of the pressure in  $V = V(N_1, N_2, p, T)$ . With the variables  $N_1, N_2, p$  and  $T$  given fixed values, the corresponding volume can now be determined from the equation of state and so the Gibbs free energy which is found for these values of  $N_1, N_2, V$  and  $T$  is also the Gibbs free energy as a function of  $N_1, N_2, p$  and  $T$ . This replacement of variables  $V$  and  $p$  in a scheme to

calculate  $G(N_1, N_2, p, T)$  implicitly from  $G(N_1, N_2, V, T)$  is further complicated by the form of the equation of state itself. From equations (2), (8) and (19), it is seen that the  $K_{\alpha\beta}$  which determine the dipolar contribution to the pressure must be known as a function of the densities  $\rho_1, \rho_2$  and temperature  $T$ . Unfortunately these properties of the  $K_{\alpha\beta}$  are not available in closed form. Therefore an iteration scheme was devised to solve the equations for the total number density (at constant composition). This then gives the volume from  $V = N/\rho$  as required by the equation of state to give the fixed value of the pressure. The rest of this Chapter is concerned with the actual details of the calculation for the (implicit) pressure dependence of the Gibbs free energy of a mixture of dipolar hard spheres. The results are given in terms of certain excess free energies to be defined in the following Section.

#### 4. Numerical Methods

##### 4.1 Preliminary Investigation

From equations (3), (11) and (20) of Section 2, it can be seen that the Gibbs free energy of a mixture of dipolar hard spheres is equal to a hard sphere term plus a dipolar term which is in excess of the hard sphere contribution. The hard sphere contribution to the Gibbs free energy is a straightforward substitution of the densities  $\rho_1$  and  $\rho_2$  into equations (8) and (11). In contrast to this simple calculation of the hard sphere contribution, the calculation of the dipolar term in equation (20) is not so straightforward. The problem lies in the calculation of the  $K_{\alpha\beta}$ 's which are employed in equation (20). For the binary mixture case, this specifically reduces to finding the solutions  $K_{11}$ ,  $K_{22}$  and  $K_{12}$  ( $= K_{21}$ , by symmetry) of three coupled algebraic equations

(cf. equation (55) of Chapter 2). Many unsuccessful methods of solving this set of equations were tried until the present technique used in this thesis was evolved. The present method of solution has proved very stable at all densities and for ratios of diameter of species two to diameter of species one up to three. The details will be given later in this Section, but it should be mentioned here that the problem of solving for the roots of a system of equations in more than one independent variable was more complicated than first thought by the author. Indeed, comfort is found in the words of Acton (1975): "A search for a lost dog on a foggy country lane is much easier than a search for the same dog in a foggy field, and if the lost pet is a squirrel in the forest, his three-dimensional capability complicates the task by still another order of magnitude. As for finding ghosts, reputed to have at least four-dimensional existences, we defer to our British colleagues, pleading inexperience."

It is interesting to consider first the solution of the corresponding equations for a pure component fluid of dipolar hard spheres of species one. Such an example serves a twofold purpose: firstly, an efficient one-dimensional search routine can be envisaged which would solve a single algebraic equation for  $K$ , or some more convenient variable (to be introduced soon). Secondly, there are closed-form expressions for the dipolar contributions to the internal energy, Helmholtz free energy, Gibbs free energy and the pressure for the case of a single component fluid (Adelman and Deutch, 1973). Thus a numerical study of the single component self-consistency equation for  $K$  might offer a generalization of the associated one-dimensional algorithm for use in the binary mixture problem. For

binary mixtures, an efficient algorithm is required to search the three-dimensional space of  $(K_{11}, K_{22}, K_{12})$  in order to find a solution of the self-consistency equations. Furthermore, the calculation of the dipolar contributions to the above thermodynamic functions would be helpful if any numerical integrations or differentiations were to be developed for the evaluation of the corresponding quantities in the mixture case. The accuracy of the procedures employed in the latter calculation could then be determined from a direct comparison of the numbers obtained for mole fraction zero (or unity).

The algebraic equation to be solved in the case of a pure fluid is

$$\frac{4\pi}{3} \beta m^2 \rho = Q(2K\rho^*) - Q(-K\rho^*) , \quad (21)$$

where

$$\rho^* = \frac{\pi}{6} \rho R^3 ,$$

and

$$Q(\xi) = (1 + 2\xi)^2 / (1 - \xi)^4 .$$

$Q(\xi)$  is recognised as the inverse compressibility of a fluid of hard spheres at density  $\xi$ . Equation (21) was originally determined by Wertheim (1971) but can also be derived from equations (55) of Chapter 2 in the limit  $\rho_2 \rightarrow 0$ , and dropping the subscripts on the variables  $m_1, \rho_1, K_{11}$  after the limit has been taken. Numerical results for the gas-liquid phase equilibria in the pure fluid have been reported by Rushbrooke et al. (1973) and Sutherland et al. (1974). The results of these investigations essentially show that the thermodynamic properties of a dipolar

fluid in the Mean Spherical Approximation are intermediate between those properties described by the Onsager model (Sutherland et al., 1974) and by the thermodynamic perturbation theory (Rushbrooke et al., 1973). The quantitative comparisons are made from an examination of the coexistence region for liquid-gas equilibrium predicted from each model. The details of the dipolar contribution to the various thermodynamic variables will be given shortly. However, such terms are dependent on  $K$  as a function of  $\beta$ ,  $m$  and  $\rho$ , and so equation (21) must be solved (numerically) for  $K$  as a function of the product  $\beta m^2 \rho$ . Introducing the reduced inverse temperature  $\beta^* = \beta m^2 / R^3$ , the reduced density  $\rho^* = \pi \rho R^3 / 6$  and  $\xi = \rho^* K$  reformulates equation (21) as

$$8 \beta^* \rho^* = Q(2\xi) - Q(-\xi) \quad . \quad (22)$$

A direct interpretation of equation (22) is: given  $\beta^*$  and  $\rho^*$  what is the root  $\xi$  of the above algebraic equation. Thus, a program was written which used Newton's algorithm (Conte and de Boor, 1972) to determine the root of equation (22). For the initial investigation, the calculation was done on a HP 9830 digital calculator using Basic Language. Solutions for  $\xi$  were found efficiently and accurately within the convergence criteria that  $|\xi_{\text{new}} - \xi_{\text{old}}| < 10^{-7}$ . Since the  $\xi$  were found to be of the order of  $10^{-1}$ , this tolerance ensured the solution was known to at least six places (after the decimal point) and the corresponding function,  $8\beta^*\rho^* - (Q(2\xi) - Q(-\xi))$ , was often less than  $10^{-10}$  for the value of  $\xi_{\text{new}}$  satisfying the convergence criterion.

It should be mentioned that the initial starting point was taken from the low density limit of  $K = \beta m^2 / (3 R^3)$  and the density  $\rho^*$  as

$$\xi_{\text{start}} = \beta^* \rho^* / 3 \quad ,$$

or the previous  $\xi$  bootstrapped for a new density value along an isotherm. The initial convergence rate was slow for the first density point, as indicated by ten to twenty iterations when using

$\xi_{\text{start}} = \beta^* \rho^* / 3$ , but improved significantly once the bootstrap operated where two to five iterations were needed for convergence. The changes in density  $\rho^*$  along an isotherm were .025 or .05 units depending on the particular run.

In order to check these results and the efficiency, another program (again in Basic on the HP 9830) was written to solve the equation (22) using the binary chop search method (Acton, 1970). The same starting value for  $\xi_{\text{start}} = \beta^* \rho^* / 3$  was used for the first density point along an isotherm ( $\beta^* = \text{constant}$ ) and the interval of search, denoted by  $\Delta \xi$ , halved until  $\Delta \xi < 10^{-7}$ . Comparable results were obtained for both methods as far as accuracy:- although the binary search took slightly more time than the Newton algorithm. Both programs were then augmented by subroutines to calculate the dipolar contributions to the pressure, Helmholtz and Gibbs free energies, the expressions for which were given by Adelman and Deutch (1973). The pressures at each density point along the isotherms  $\beta^* = .2384, .2251, .21173$  and  $.1984$  were calculated and agreed within errors associated with the digitization process with the digitized data taken from Figure 4 in the published work of Sutherland et al. (1974). This computation was not primarily done to check the single component calculations but rather to find a successful procedure in the one-dimensional problem of root-solving for the single component case, which could then be generalized to an efficient search routine in the three-dimensional problem of root-solving for the two-component case.

In addition to these procedures, a hybrid search program was tested, i.e., a biased search routine with a carefully chosen step size. A binary chop method was used to roughly locate the root until the step size  $\Delta\xi$  reached a sufficiently small value (arbitrarily chosen as  $10^{-3}$ ), at which point the program automatically invoked the more efficient Newton algorithm to finish the search for the root more rapidly.

All the above search routines seeking the root of a function of a single variable were equivalent: each located the root according to a common convergence criterion, and in roughly the same time interval.

Before reviewing the applicability of the generalizations of the various search routines to solving a set of dependent equations, it is appropriate at this point to introduce the reduced forms of the thermodynamic functions for pure dipolar fluids. The reduced parameters for the inverse temperature  $\beta^*$ , number density  $\rho^*$ , pressure  $P^*$ , internal energy per unit volume  $E^*$ , and Helmholtz (Gibbs) free energy per unit volume  $A^*(G^*)$  are

$$\beta^* = \beta m^2 / R^3 ,$$

$$\rho^* = \pi \rho R^3 / 6 ,$$

$$P^* = \pi R^6 P / (48 m^2) ,$$

$$E^* = \pi R^6 E / (48 m^2 V) ,$$

$$A^* = \pi R^6 A / (48 m^2 V) ,$$

and

$$G^* = \pi R^6 G / (48 m^2 V) . \quad (23)$$

In terms of these reduced variables the compressibility factor  $Z = PV/NkT$  and the Gibbs free energy in units of  $NkT$  can be written as

$$Z = 8\beta^* \rho^* / \rho^* , \quad (24)$$

$$G/NkT = -8\beta^* G^* / \rho^* . \quad (25)$$

The closed-form expressions for the dipolar contribution to the pressure and the free energies (Rushbrooke et al, 1973) can be rewritten in the reduced units of equation (23) as:

$$\Delta P^* = -\rho^{*2} K + \frac{(\rho^* K)^2}{\beta^*} \left[ \frac{(1+\rho^* K)^2}{(1-2\rho^* K)^4} + \frac{(2-\rho^* K)^2}{8(1+\rho^* K)^4} \right] , \quad (26)$$

$$\Delta E^* = -\rho^{*2} K , \quad (27)$$

$$\Delta A^* = -\frac{(\rho^* K)^2}{\beta^*} \left[ \frac{(1+\rho^* K)^2}{(1-2\rho^* K)^4} + \frac{(2-\rho^* K)^2}{8(1+\rho^* K)^4} \right] , \quad (28)$$

and

$$\Delta G^* = -\rho^{*2} K . \quad (29)$$

The details of the derivation of these equations are given in Rushbrooke et al. (1973). However all are based on the availability of an analytic expression for  $\Delta A/V$ , which is obtained via an integration by parts of the internal energy density  $\Delta E/V$  with respect to  $\beta m^2/R^3$ . From equations (26) - (29), it is clearly seen that these dipolar contributions to the thermodynamic functions are easily evaluated on a calculator once  $\rho^*K$  is known for the particular  $\rho^*$ ,  $\beta^*$  being studied. This combination of an efficient search routine to solve equation (22) for  $\rho^*K$  (given  $\rho^*$  and  $\beta^*$ ) and the direct substitution of  $\rho^*$ ,  $\beta^*$  and  $\rho^*K$  into closed expressions to determine the thermodynamic state was originally thought to lend itself to straightforward generalization to the binary mixture case.

However, a generalization of the one-dimensional search routines to find the simultaneous zeros of three algebraic coupled equations was not achieved. The major difficulties were associated with the extra freedom offered to the searching algorithm in three dimensions. Each such searching procedure was to solve equation (86) of Chapter 2 for the simultaneous zeros  $K_{11}$ ,  $K_{22}$  and  $K_{12}$  as a function of the parameters  $\rho_1$ ,  $\rho_2$ ,  $m_1$ ,  $m_2$ ,  $\beta$ ,  $R_1$  and  $R_2$ .

Before giving the applications of the search routines, it is necessary to discuss the reduced parameters and the choice of independent parameters in the binary mixture case. The dipole moments and molecular diameters of each species are now used to define a reduced inverse temperature  $\beta^*$  and a reduced density  $\rho^*$ ,

defined by

$$\beta_{\alpha}^* = \beta m_{\alpha}^2 / R_{\alpha}^3 \quad (30)$$

and

$$\rho_{\alpha}^* = \frac{\pi}{6} \rho_{\alpha} R_{\alpha}^3, \quad (31)$$

where  $\rho = \rho_1 + \rho_2$  is the total number density of the binary mixture. It is appropriate to rewrite equations (86) of Chapter 2 explicitly in terms of these reduced parameters:

$$8 \beta_1^* \rho_1^* = \phi_{11}(K_{11}, K_{22}, K_{12}),$$

$$8 \beta_2^* \rho_2^* = \phi_{22}(K_{11}, K_{22}, K_{12}),$$

and

$$8 \sqrt{\beta_1^* \beta_2^* \rho_1^* \rho_2^*} = \phi_{12}(K_{11}, K_{22}, K_{12}). \quad (32)$$

In the above equation,  $\phi_{\alpha\beta}$  is a function also of the densities and molecular diameters, i.e.,

$$\phi_{\alpha\beta}(K_{11}, K_{22}, K_{12}) = \phi_{\alpha\beta}(K_{11}, K_{22}, K_{12}; \rho_1, \rho_2, R_1, R_2), \quad (33)$$

and is given by equations (84) and (85) of Chapter 2:

$$\phi_{\alpha\beta}(K_{11}, K_{22}, K_{12}) = -\tilde{C}_{\alpha\beta}^+(0; 2\rho_1, 2\rho_2) - \tilde{C}_{\alpha\beta}^-(0; -\rho_1, -\rho_2). \quad (34)$$

It will be shown later that  $\phi_{\alpha\beta}$  is indeed only a function of  $K_{11}$ ,  $K_{22}$ ,  $K_{12}$  and  $\rho_{\alpha}^*$ , along with the ratio of the molecular diameters,  $w = R_2/R_1$ . In terms of equations (30) and (31), equation (32) can be summarized in

$$8 \sqrt{\beta_{\alpha}^* \beta_{\beta}^* \rho_{\alpha}^* \rho_{\beta}^*} = \phi_{\alpha\beta}(K_{11}, K_{22}, K_{12}; \rho_1^*, \rho_2^*, w). \quad (35)$$

The problem is to solve equation (35) for  $K_{11}$ ,  $K_{22}$  and  $K_{12}$  given  $\beta_1^*$ ,  $\rho_1^* + \rho_2^* = \xi$ ,  $m_2/m_1$ ,  $R_2/R_1$  and the mole fraction of species two,  $x$ , as independent variables. This choice of the independent variables is not unique. However it does provide sufficient information to solve the system of equations under consideration. Using  $\beta_1^*$ ,  $\xi$ ,  $m_2/m_1$ ,  $R_2/R_1$  and  $x$ , the reduced parameters in equation (35) are given as

$$\beta_1^* = \beta_1^* ,$$

$$\beta_2^* = m_2^2 R_1^3 \beta_1^* / (m_1^2 R_2^3) ,$$

$$\rho_1^* = \xi / (1 + x w^3 / (1 - x)) ,$$

and

$$\rho_2^* = \xi - \rho_1^* . \quad (36)$$

The specific details of the unsuccessful generalized search algorithms will not be given here, except to summarize some general findings. The most common feature was the failure to solve the equations (32) consistently for all values of density, composition and temperature considered. Here the molecular parameters  $m_2/m_1$  and  $R_2/R_1$  are fixed, thus specifying the relative properties of the components with respect to species one and also the degree of complexity of the search. As a general rule, the various algorithms only solved the equations in the low density-high temperature regime at all compositions considered, for values of  $m_2/m_1$  and  $R_2/R_1$  equal to unity. This deficiency in the

selected algorithms was an immediate source of concern, since the primary application was the study of liquid-liquid immiscibility where the product of  $\beta\rho$  was not small. The relaxation of the convergence criteria from the smallness of the difference

$$\phi_{\alpha\beta} - 8\sqrt{\beta_{\alpha}^* \beta_{\beta}^* \rho_{\alpha}^* \rho_{\beta}^*}$$

to a minimization of the sums of the squares of these differences did speed up the convergence in the low  $\beta\rho$  region but did not resolve the failure of the search routines to find solutions at the relevant liquid values of the  $\beta\rho$  region. The failure to find solutions at moderate and high densities for a given temperature was then thought to be caused by the "bootstrapping" method of using the solution obtained at the previous density point along the isotherm. Unfortunately, any decrease in the density increment only postponed the divergence or sometimes even hastened it if the initial trial solution was not within .1% of the true solution.

Another common source of the failure of these three-dimensional search routines, which was also investigated, was found to be due to the search being trapped in regions of local minima in the  $(K_{11}, K_{22}, K_{12})$  solution space. This effect produced oscillations in the  $K_{12}$  values for fixed values of  $K_{11}$  and  $K_{22}$ , in both the fundamental search algorithms, which are the three-dimensional star search and the three-dimensional Newton-Raphson algorithms (Acton, 1970). In order to eliminate these local minima, the program was automated such that  $(K_{11}, K_{22}, K_{12})$  were re-initialized to bias the search away from such anomalies. For the star search and the Newton algorithm, the most successful means of reinitialization was increasing the step size of the search pattern

and mixing the solutions, respectively. Unfortunately, such automaticity in the search routines was time-consuming and only partially improved the success of the algorithms to find solutions in the liquid  $\beta\rho$  regime. It should be stated here that up to this point in the computational side of the search routines, the HP 9830 was the primary tool in use. Because of the enormous amount of time being spent during a run, it was necessary to change over to the departmental PDP 11/45 computer. The calculations on the 11/45 were of the order of  $10^2$  faster than on the HP 9830. However, the fundamental result (forecast in the exploratory calculations on the 9830 calculator for the equal dipole moment and equal diameter case) was reaffirmed strongly and quickly on the computer. The generalization of any one-dimensional root searching routine to a three-dimensional procedure was not straightforward, and a more sophisticated automation of such a three-dimensional search algorithm was required to improve the rate of convergence after encounters with local minima or finding spurious roots introduced by the minimization of a sum of squared terms occurred in the search.

This lack of an efficient three-dimensional search algorithm prompted re-evaluation of the basic algorithms under consideration and further examination of Acton's philosophy on "curve-crawling strategies in several dimensions" (Acton, 1970). The application of several of these curve-crawling strategies was again disappointing in the liquid  $\beta\rho$  region, even though an effective single component system (equal diameter, equal dipole moment) was being examined. Further application of all searching routines to the slightly more general case of an equal diameter-nonequal dipole moment binary mixture was even less heartening (c.f., equations of Adelman and Deutch, 1973). The region of convergent solutions decreased dramatically.

indicating a lack of sophistication in the automation of the program, and an inefficiency of the particular algorithm for searching the three-dimensional solution space of  $(K_{11}, K_{22}, K_{33})$ . However, the equations of Adelman and Deutch (1973), which were used to check the solutions of the equations developed here, were easily solved through a one-dimensional search routine. The reduction of the equations to a single algebraic equation in terms of one unknown,  $\hat{K}$ , instead of the triad  $(K_{11}, K_{22}, K_{33})$  was possible for equal diameters only. Such a reduction is not well-defined in the nonequal diameter case, as was shown in Chapter 2. Nevertheless, a successful search routine was eventually constructed and the motivation and details are now given explicitly.

## 4.2 Final Procedures

### 4.2.1 Introduction

After much numerical experimentation, it was obvious that the three-dimensional star search was very time-consuming when it was successful, usually for low values of  $\beta p \leq .125$  with initial trial solutions aptly chosen. (The initial trial  $K_{\alpha\beta}$ 's were necessarily within .1% of the solution for the three-dimensional star procedure to work.) A similar explanation can be given for the failure of the three-dimensional Newton root-searching routine. When the initial triad solution was too far removed from the unknown solution set of zeros, the Newton search would undergo oscillations for the solution through underestimating the position of the zeros and then overcompensating for that previous error. In summary, the solution of this particular set of nonlinear equations, in which the functions change so drastically for small perturbations in the

$K_{\alpha\beta}$ 's, requires a higher order algorithm as the basis of the

search procedure than is provided by the zeroth order and first order derivatives of the three-dimensional star search and three-dimensional Newton procedures, respectively. Thus the use of a low order search algorithm should not be expected to be efficient and reliable. This leads to a reinterpretation of equations in terms of new dependent and independent variables (Freasier, 1976).

Conceptually, this new approach is seen most readily in the single component case. Equation (22) was originally interpreted as an equation which was to be solved for  $K\rho^*$  as a function of  $\beta m^2 \rho$  necessitating an iterative routine. Alternatively, the same equation gives  $\rho^*$  as a function of  $K\rho^*$  and  $\beta^*$  in the form of a simple algebraic equation:

$$\rho^* = \{ Q(2K\rho^*) - Q(-K\rho^*) \} / 8\beta^* \quad (37)$$

where  $0 < K\rho^* < 1/2$ , and  $\beta^* > 0$ . Those values of  $K\rho^*$  giving  $\rho^* > 1$  are not considered. This set of variables  $\beta^*$ ,  $\rho^*$  and  $K\rho^*$  then allows the thermodynamic state to be calculated from substitution into equations (23) - (29). The extension of this reinterpretation of dependent and independent variables for the equations describing binary mixtures is complicated by the number and choice of independent variables.

#### 4.2.2 Independent Variables

For binary mixtures, the input parameters could be formally chosen as  $K_{11}^* = \frac{\pi}{6} \rho_1 K_{11} R_1^3$ ,  $K_{22}^* = \frac{\pi}{6} \rho_2 K_{22} R_2^3$ ,  $\Delta = 1 - K_{12}^2 / (K_{11} K_{22})$  and  $\beta^* = \beta m_1^2 / R_1^3$ . In addition to such a set of variables, the molecular description of the mixture provided the values of the

ratios of dipole moments  $m_2/m_1$  and diameters  $R_2/R_1$ . For known values of  $K_{11}^*$ ,  $K_{22}^*$ ,  $\Delta$  and  $\beta^*$  the densities could be determined from the equations (38):

$$\begin{aligned}\rho_1^* &= \frac{\pi}{6} \rho_1 R_1^3 = \Phi_{11}(K_{11}^*, K_{22}^*, \Delta) / (8\beta^*) , \\ \rho_2^* &= \frac{\pi}{6} \rho_2 R_2^3 = \Phi_{22}(K_{11}^*, K_{22}^*, \Delta) / (8\beta^*) ,\end{aligned}\quad (38)$$

where  $\beta_2^*$  is determined from  $\beta^*$ ,  $m_2/m_1$  and  $R_2/R_1$  in

$$\beta_2^* = m_2^2 R_1^3 \beta^* / (m_1^2 R_2^3) .$$

The functions  $\Phi_{\alpha\beta}(K_{11}^*, K_{22}^*, \Delta)$  are defined in terms of  $\phi_{\alpha\beta}$  in equation (32) as

$$\Phi_{\alpha\beta} = \phi_{\alpha\beta}(K_{11}, K_{22}, K_{12}). \quad (39)$$

Thus the density  $\xi = \rho_1^* + \rho_2^*$  and composition  $x = \rho_2^* / (\rho_1^* + \rho_2^*)$  can be determined from  $K_{11}^*$ ,  $K_{22}^*$  and  $\Delta$  for a given reciprocal temperature  $\beta^*$ . In other words,  $K_{\alpha\beta}$  is known for a given density, composition and temperature if  $K_{11}^*$ ,  $K_{22}^*$  and  $\Delta$  are chosen so as to satisfy the three equations. It can be shown that inversion of the definitions of  $K_{\alpha\beta}^*$  and  $\Delta$  gives

$$K_{11} = K_{11}^* / \rho_1^* ,$$

$$K_{22} = K_{22}^* / \rho_2^* ,$$

and

$$K_{12} = \sqrt{K_{11}^* K_{22}^* (1 - \Delta) / (\rho_1^* \rho_2^*)} . \quad (40)$$

Before giving details of the choice of  $K_{\alpha\beta}^*$  and  $\Delta$  at a given temperature, it is necessary to reconsider the application of the results. As shown earlier in Section 3, the theory of immis-

cibility in mixtures calls for the calculation of the composition dependence of the Gibbs free energy at constant pressure and temperature. Therefore, the symmetry in the above strategy must be broken in order to allow the composition,  $x$ , to be used as an input variable rather than, say,  $K_{22}$  or  $\Delta$ . In other words, the  $K_{\alpha\beta}$  are now constrained to be found as a function of the independent composition variable  $x$ , rather than the  $K_{\alpha\beta}$  being calculated for unspecified values of  $x$ , as per the original equation (38) for different choices of  $K_{\alpha\beta}^*$  and  $\Delta$ . Such a constraint manifests itself in the replacement of  $K_{\alpha\beta}^*$  and  $\Delta$  by  $x$  and  $K_{11}^*$  as independent variables in the procedure leading to equations (38).

#### 4.2.3 Iteration Procedures

The following strategy is adopted. For fixed values of  $m_2/m_1$ ,  $R_2/R_1$ ,  $\beta^*$  and  $x$ ,  $K_{11}^*$  is preset at a small positive value,  $K_{11}^* < 0.25$ . Equations (32) are then manipulated to provide two further equations which are now used to solve for  $K_{22}^*$  and  $\Delta$  at the particular value of  $K_{11}^*$  being considered. The actual solution of these equations consists of a doubly nested one-dimensional iteration routines for  $K_{22}^*$  and  $\Delta$  until the values of  $K_{22}^*$  and  $\Delta$  are found which, together with  $K_{11}^*$ , satisfy the manipulated equations to within some given tolerance level. Then the densities  $\rho_\alpha^*$  can be found from equation (38),  $K_{\alpha\beta}$  from equation (40), and therefore the  $K_{\alpha\beta}$ 's are given as a function of  $\rho_1^*$ ,  $\rho_2^*$ , and  $\beta^*$  (or equivalently  $\xi$ ,  $x$  and  $\beta^*$ ) if the whole strategy outlined above is repeated for different input values of  $K_{11}^*$ . Before detailing such a strategy, the success of this approach should be emphasized. Given  $0 < K_{11}^* < 0.25$ ,  $1 < m_2/m_1 < 1.5$  and  $1 < R_2/R_1 < 3$ , it was found that the above nested search

routine solved for  $K_{22}^*$  and  $\Delta$  within two to ten iterations at each level. Convergence was given by a tolerance of  $10^{-6}$  on the values of  $K_{22}^*$  and  $\Delta$ . The disadvantages of the previous approaches to obtaining the density, composition and density dependences of the  $K_{\alpha\beta}$  via a three-dimensional search procedure have now been eliminated. The details of this efficient search algorithm will now be given.

A preliminary step in the numerical work is the substitution of the following factorized form of  $\Phi_{\alpha\beta}(K_{11}^*, K_{22}^*, \Delta)$  into equations (32). From equation (34) and equation (84) of Chapter 2, it can be shown that the  $\Phi_{\alpha\beta}$  can be written as:

$$\Phi_{11}(K_{11}^*, K_{22}^*, \Delta) = K_{11}^* F_1(K_{11}^*, K_{22}^*, \Delta), \quad (41)$$

$$\Phi_{22}(K_{11}^*, K_{22}^*, \Delta) = K_{22}^* F_2(K_{11}^*, K_{22}^*, \Delta) \quad (42)$$

and

$$\Phi_{12}(K_{11}^*, K_{22}^*, \Delta) = \sqrt{K_{11}^* K_{22}^* (1-\Delta)} F_3(K_{11}^*, K_{22}^*, \Delta), \quad (43)$$

where  $F_\alpha(K_{11}^*, K_{22}^*, \Delta)$  is  $\Phi_{\alpha\beta}$  divided by the appropriate combination of  $K_{11}^*$ ,  $K_{22}^*$  and  $\Delta$ . Equation (32) can now be rewritten in terms of the  $F_\alpha$  as

$$8 \beta_1^* \rho_1^* = K_{11}^* F_1(K_{11}^*, K_{22}^*, \Delta), \quad (44)$$

$$8 \beta_2^* \rho_2^* = K_{22}^* F_2(K_{11}^*, K_{22}^*, \Delta) \quad (45)$$

and

$$8 \sqrt{\beta_1^* \beta_2^* \rho_1^* \rho_2^*} = \sqrt{K_{11}^* K_{22}^* (1-\Delta)} F_3(K_{11}^*, K_{22}^*, \Delta). \quad (46)$$

Equations (44) and (45) can be divided to give the following expression for  $K_{22}^*$ :

$$K_{22}^* = \frac{m_2^2 \times K_{11}^* F_1(K_{11}^*, K_{22}^*, \Delta)}{m_1^2 (1-x) F_2(K_{11}^*, K_{22}^*, \Delta)}. \quad (47)$$

A further equation for  $\Delta$  in terms of  $K_{11}^*$ ,  $K_{22}^*$  and  $\Delta$  can be obtained from equations (44)-(46): the right hand sides of these equations are substituted for  $\beta_1^* \rho_1^*$ ,  $\beta_2^* \rho_2^*$  and  $\sqrt{\beta_1^* \beta_2^* \rho_1^* \rho_2^*}$  in the identity  $(\beta_1^* \rho_1^*) (\beta_2^* \rho_2^*) = (\sqrt{\beta_1^* \beta_2^* \rho_1^* \rho_2^*})^2$ . This leads to an equation for  $\Delta$  in terms of  $K_{11}^*$ ,  $K_{22}^*$  and  $\Delta$ , and this is given as equation (48).

$$\Delta = 1 - \frac{F_1(K_{11}^*, K_{22}^*, \Delta) F_2(K_{11}^*, K_{22}^*, \Delta)}{(F_3(K_{11}^*, K_{22}^*, \Delta))^2}. \quad (48)$$

Equations (47) and (48) are used as iteration schemes to update the values of  $K_{22}^*$  and  $\Delta$  from the previously known values of  $K_{22}^*$ ,  $\Delta$  and  $K_{11}^*$  (held fixed throughout the schemes until a solution for that particular  $K_{11}^*$  is found). The very first trial solution is given by the input value of  $K_{11}^*$ , and the unknowns  $K_{22}^*$  and  $\Delta$  are approximated by

$$K_{22}^* = 0,$$

and

$$\Delta = 1 - \frac{R_1^3 R_2^3}{R_{12}^6}. \quad (49)$$

The resulting solutions for  $K_{22}^*$  and  $\Delta$  are then used as starting values for  $K_{22}^*$  and  $\Delta$  in the next value of  $K_{11}^*$  considered. The convergence criteria used were

$$\left| 1 - (1 - \Delta) F_3^2 / (F_1 F_2) \right| < 10^{-6} ,$$

and

$$\left| K_{22}^* - (m_2^2 x / ((1-x)m_1^2)) K_{11}^* F_1 / F_2 \right| < 10^{-6} .$$

These tolerance levels allowed reasonably accurate (correct to sixth decimal place) values of  $K_{22}^*$  and  $\Delta$  to be obtained from up to five iterations, at the most, in each hierarchy of convergence for  $\Delta$  and  $K_{22}^*$ . For equal diameter, these solutions were checked with those of a program written to solve the Adelman-Deutch equations. The agreement was within the allowed tolerance level. Thus, the primary aim of developing an efficient algorithm to solve the self-consistency equations for a binary mixture of nonequal dipole moments and nonequal diameters has been accomplished through the above procedure leading to the iteration schemes in equations (47) and (48). The  $K_{\alpha\beta}$  are now known as functions of density, composition and temperature from equations (38) and (40), in a somewhat arbitrary fashion. According to equation (16), the dipolar contribution to the internal energy,  $\Delta E$ , is essentially a sum over the  $K_{\alpha\beta}$  and so is known at the particular total density  $\xi$  and composition  $x$  for given values of  $m_2/m_1$ ,  $R_2/R_1$  and  $\beta$ . Here  $\xi$  is found from  $\rho_1^*$  to be

$$\xi = \rho_1^* (1 + x R_2^3 / ((1-x) R_1^3)) , \quad (50)$$

eliminating the need to use the second equality in equation (38) to obtain  $\rho_2^*$  and then using  $\xi = \rho_1^* + \rho_2^*$  to obtain the total volume density.

### 4.3 Calculation of Dipolar Contributions to the Energy and Helmholtz Free Energy

At this point, further refinements have to be made to the method of defining the  $K_{\alpha\beta}$  in equations (38) and (40) so that the dipolar contributions to the Helmholtz free energy, pressure and Gibbs free energy can be calculated. The calculations of these thermodynamic quantities as functions of composition, density and temperature are required in order to determine the miscibility or immiscibility of a binary mixture through the composition dependence of the Gibbs free energy at constant temperature and pressure. However, the important step in such a calculation is the evaluation of the dipolar internal energy for different reciprocal temperatures at constant density,  $\xi$ , and composition,  $x$ . Obviously, the initial approach of using equation (40) to determine the  $K_{\alpha\beta}$  using the  $\rho_{\alpha}^*$  as calculated from equation (38) would not ensure constancy of  $\xi$  and  $x$  for a series of  $\beta^*$ 's. The standard solution employing the procedure leading to equations (47) and (48) already imposes a constraint on  $x$  which is used as an independent variable. However, for a series of different  $\beta^*$ 's,  $\xi$  as obtained from equation (50) may vary enormously for a fixed value of  $K_{11}^*$  if equation (38) is used to solve for  $\rho_1^*$ . This difficulty is circumvented in the following choice of independent variables.

For the application of the density, composition and temperature properties of the  $K_{\alpha\beta}$  to mixing properties, it is necessary to solve equations (44)-(46) for  $K_{\alpha\beta}$  at fixed values of  $\rho_1^*$ ,  $\rho_2^*$ ,  $m_2/m_1$  and  $R_2/R_1$ . For a given value of  $K_{11}^*$  in the domain  $0 < K_{11}^* < .25$ , equations (44)-(45) can be solved using equations (47) and (48) as iteration schemes to determine  $K_{22}^*$  and  $\Delta$ . This procedure assumes the independent variables

to be  $K_{11}^*$ ,  $m_2/m_1$ ,  $R_2/R_1$  and  $x$ .  $K_{11}^*$ ,  $K_{22}^*$ ,  $\Delta$ ,  $x$  and  $R_2/R_1$  then allow the right-hand sides of equations (44)–(46) to be determined, i.e., products of  $\beta_1^* \rho_1^*$  and  $\beta_2^* \rho_2^*$  are known. This offers  $\rho_1^*$  as a function of the independent variable  $\beta_1^*$ , which is seen explicitly in equation (38) when it was convenient to have temperature as an independent variable. Alternatively  $\beta_1^*$  is given by the relationship

$$\beta^* = \beta_1^* = K_{11}^* F_1(K_{11}^*, K_{22}^*, \Delta) / \rho_1^* , \quad (51)$$

which allows the total density and composition (i.e.,  $\rho_1^*$  and  $x$ ) to be chosen as independent variables, thereby fixing the reciprocal temperature through equation (51). At any particular  $K_{11}^*$ , the  $K_{\alpha\beta}$  are given by equation (40), where the densities  $\rho_1^*$  and  $\rho_2^*$  are input parameters, constrained only by the following relation in equation (52).

$$\rho_2^* = \rho_1^* x R_2^3 / ((1-x) R_1^3) . \quad (52)$$

Equations (51), (52) and the procedure of solving equations (44)–(46) then allow the dipolar contribution to the internal energy,  $\Delta E$ , to be determined as a function of specified density and composition. This, in turn, permits the inverse temperature quadrature of equation (16) to be accomplished in order to obtain the dipolar contribution to the Helmholtz free energy. In reduced units and scaled variables, the internal and Helmholtz free energies can be written:

$$\begin{aligned} \Delta E^* &= \pi R_1^6 \Delta E / (48 m_1^2 V) \\ &= - \left[ \rho_1^* K_{11}^* + \rho_2^* K_{22}^* m_2^2 R_1^6 / (m_1^2 R_2^6) \right. \\ &\quad \left. + 2 \sqrt{\rho_1^* \rho_2^* K_{11}^* K_{22}^* (1-\Delta)} m_2^2 R_1^3 / (m_1^2 R_2^3) \right] , \quad (53) \end{aligned}$$

and

$$\begin{aligned}\Delta A^* &= \pi R_1^2 \Delta A / (48 m^2 V) \\ &= \beta^{*-1} \int_0^{\beta^*} d\beta^{*'} \Delta E^*(\beta^{*'}) .\end{aligned}\quad (54)$$

The integral over  $\beta^{*'}$  in equation (54) was done using Gaussian quadrature for an arbitrary interval  $(0, \beta^*)$ . Then the integral is approximated by a finite sum:

$$\int_0^{\beta^*} d\beta^{*'} \Delta E^*(\beta^{*'}) = \frac{\beta^*}{2} \sum_{i=1}^n w_i \Delta E^*\left(\frac{1}{2}\beta^*(x_i+1)\right), \quad (55)$$

where  $x_i$  and  $w_i$  are the  $i^{\text{th}}$  zero of the Legendre polynomial of order  $n$  (Abramowitz and Stegun, 1968), and its associated weight, respectively. The transformation  $y_i = \frac{1}{2}\beta^*x_i + \frac{1}{2}\beta^*$  has been applied so that the domain of  $\beta^{*'}$ ,  $0 < \beta^{*' < \beta^*$ , coincides with the domain  $-1 < y < 1$  over which the Legendre polynomials

$P_n(y_i)$  are defined. The choice of  $n$  is to be optimized for the particular integrand being considered. In equation (55),  $\Delta E^*$  must be evaluated at the associated zeros,  $y_i$ , which are effectively predetermined reduced temperatures  $\beta^{*'}$ . Thus, the arbitrarily calculated  $\beta^*$  values of  $\Delta E^*$  must be interpolated accurately to give  $\Delta E^*$  at  $y_i$ . The error of equation (55) is a function of the domain of integration,  $\beta^*$ , the number of points used,  $n$ , and the maximum slope of the function  $\Delta E^*(y)$  over  $-1 < y < 1$ . The error is given by  $R_n$  (Abramowitz and Stegun, 1968) where

$$R_n = \frac{(2\beta^*)^{2n+1}(n!)^4}{(2n+1)!((2n)!)^3} \max_{-1 < y < 1} \left\{ \frac{d^{2n} \Delta E^*}{dy^{2n}} \right\}. \quad (56)$$

We have not evaluated the remainder  $R_n$  explicitly. However some degree of confidence for small  $R_n$  is given by the smooth behaviour of  $\Delta E^*$  which is quadratic in  $\beta^*$  for small  $\beta^*$  and then essentially linear in  $\beta^*$  as  $\beta^*$  increases. Unfortunately, the error analysis is complicated by the  $\Delta E^*$  not being known at the required  $y_i$ , at which points  $\Delta E^*$  was obtained via a Lagrange interpolation procedure. In order to minimize any error initiated in the interpolation routine, the orders of the Lagrange interpolation formula and the Gaussian quadrature formula were varied until the  $\Delta E^*$  value and  $\Delta A^*$  quadrature were minimized. For equal diameters, these calculated values were compared to the analytic forms given by the results of Adelman and Deutch (1973) which are effectively equations (27) and (28) evaluated at rescaled values of  $\beta^*$ ,  $\rho^*$  and  $K^* = K \rho^*$ . From Table 1, it can be seen that the choice of the number of interpolation points which reduced the error in  $\Delta E^*$  was confined to the domain five, six, or seven. From a study of the equal dipole moment and equal diameter case, it was shown that an eight point Gaussian quadrature on the values of  $\Delta E^*$  which were interpolated from a table using six point formula gave agreement to the sixth decimal place with the formulae of Adelman and Deutch (1973). Also from Table 1, it can be shown that, as  $\beta^*$  increases, the number of points made available to the table of interpolated values also increases the error of the interpolation procedure. Table 1 is a representative of numerous pages of computer print-out, not all of which are required here. A thorough examination of the comparison between these dipolar contributions to the internal and Helmholtz free energies, and the pressure leads to the choice of optimal parameters to be eight point quadrature on the points which are selected by a six point interpolative procedure.

The details of selection of  $\Delta E^*$  values (and hence  $\beta^*$  from equation (51)) as entries in the table are now discussed. For large values of  $\beta^*$ , it was originally thought that the errors in the interpolation routine would be minimized if more information on  $(\beta^*, \Delta E^*)$  was available in the form of a larger table for  $\Delta E^*$ . Interpolations about the quadrature points, not necessarily included in the table as entries themselves, were obtained as a function of the  $\beta^*$  grid spacing. Unfortunately, the non-uniformity of the  $\beta^*$  grid, which arises from the uniformity of the  $K_{11}^*$  input values, gives rise to considerable errors in the interpolation of quadrature points using small  $\beta^*$  grid sizes in the  $\Delta E^*$  table. For the special case of  $m_2 = m_1$  and  $R_2 = R_1$ , errors of the order of  $10^{-3}\%$  were found for the tabulated values of  $\Delta E^*$  (given by forty values of  $K_{11}^*$  in steps of .005) when a six point Lagrange interpolation scheme on a set of forty points was used. In other words,  $\Delta E^*$  at this particular density,  $\xi = \pi/10$  and  $x = .5$ , could be calculated, correct to the sixth decimal place  $\pm .000001$  for  $\beta = .1$  to 4.0 in steps of .1. As the number of points in the table of  $\Delta E^*$  values increased, the loss in the number of significant figures increased until for a table of eighty entries, the error in  $\Delta E^*$  had increased to  $\pm .00001$ , a factor of ten above the absolute error for the table containing approximately forty entries, mainly due to roundoff error. Thus it was decided to use the table of approximately forty values of  $\Delta E^*$  on which the choice of a six point interpolation scheme was to be tested. The values of the order of the interpolation ranged from three to ten, given a common table of values. It was found that the three point interpolation scheme was totally unsatisfactory,

giving a maximum absolute error of  $20 \times 10^{-6}$  in  $\Delta E^*$  at  $\beta^* = 3.4$ . In order to calculate  $\Delta E^*$  correct at least to the sixth decimal place (this criterion is compatible with the values of the reduced pressure being multiples of  $461 \times 10^{-4}$ ) values for the order of the interpolation scheme were six to ten. The higher order schemes were eliminated on account of the extra time involved, leaving six as the optimal order of the interpolation scheme. Details of this effect are provided in Table 1. In fact, the number of points in the table of  $\Delta E^*$  which optimizes the information of the curve  $(\beta^*, \Delta E^*)$  about the interpolation point can be changed from forty to thirty-seven without loss in precision for the interpolated value. Thus Table 1 is also the summary of results for thirty-seven points. The choice of the number of points in the range thirty to forty seems to optimize the geometry of the curve  $\Delta E^*$  versus  $\beta^*$  in order to calculate  $\Delta E^*$  at any unknown  $\beta^*$  within the table. Since  $\beta^*$  and  $\Delta E^*$  are calculated directly in terms of the solution  $(K_{11}^*, K_{21}^*, \Delta)$  according to equations (51) and (52), the  $\beta^*$  grid is implicitly dependent on the  $K_{11}^*$  grid. Thus the actual table entries of  $\Delta E^*$  as a function of  $\beta^*$  are ultimately dependent on the value of  $K_{11}^*$  at each entry in the table. The criterion for the correct  $K_{11}^*$  grid which gives a table of  $\Delta E^*$  values at approximately evenly spaced values of  $\beta^*$  can be developed from the following investigation. Consider the table of  $\Delta E^*$  (and  $\beta^*$ ) values generated by an array of  $K_{11}^*$  values of the form  $K_{11}^*(i) = i \Delta K_{11}^*$ . Here  $\Delta K_{11}^*$  is a positive constant and  $i = 1, 2, \dots, n$  where  $n$  is the number of entries in the table of  $\Delta E^*$  and  $\beta^*$  for each  $K_{11}^*$  considered under the equal grid size of  $\Delta K_{11}^*$ . If  $\Delta K_{11}^*$  was too small,  $\Delta K_{11}^* < .001$ , an unmanageable table size of  $n \sim 1000$  was required to cover the range of  $\beta^*$  being considered.

On the other extreme, for  $\Delta K_{11}^* > .1$ , the table yielded non-physical values of  $\beta^*$  ( $\beta^* > 500$ ), and of  $K_{11}^*$  and  $K_{22}^*$  for the liquid state. Solutions of physical interest for the dipolar fluid are taken as those  $K_{11}^*$ ,  $K_{22}^*$  and  $\Delta$  values which give the matrix  $\tilde{q}_{\alpha\beta}(0)$  as positive definite (Baxter, 1970; 1975) which is a requirement that Baxter's equations can be solved. This is an extension of the negative density solution of the Percus-Yevick equation for hard sphere fluids offered by Wertheim (1971), which is necessary to solve the pure dipolar fluid equations. This competitive effect between  $\Delta K_{11}^*$  and  $n$  resulted in the increment  $\Delta K_{11}^*$  being chosen in a more ad hoc fashion to give essentially uniformity in the changes of the calculated  $\beta^*$  values rather than linear increments in  $K_{11}^*(1)$  through  $\Delta K_{11}^*$  being constant. The initial value of  $K_{11}^*$  was fixed at  $d_i$  (usually  $d_i = .001$ ) and  $\beta^*$  values calculated for  $K_{11}^* = d_i$  and  $K_{11}^* = 2 d_i$ . These values of  $\beta^*$  were then used to linearly extrapolate  $K_{11}^*(1)$  to a value which approximately gave the increment in  $\beta^*$  required. If  $\beta_1^{**}$  and  $\beta_2^{**}$  are the  $\beta^*$  values at  $d_i$  and  $2 d_i$ , respectively, and  $\Delta\beta^*$  the desired  $\beta^*$  table increment, then the increment  $\Delta K_{11}^*$ , equivalently  $K_{11}^*(2)$ , is given by

$$K_{11}^*(2) = 2d_i + d_i (\Delta\beta^* - \beta_2^{**}) / (\beta_2^{**} - \beta_1^{**}). \quad (57)$$

$\beta^*$  and  $\Delta E^*$  are now calculated at  $K_{11}^* = 0$  (where both vanish in the high temperature limit) and  $K_{11}^* = \Delta K_{11}^*$ , namely  $\beta_1^* = 0$ ,  $\Delta E_1^* = 0$  and  $\beta_2^* = \beta^*(\Delta K_{11}^*)$ ,  $\Delta E_2^* = \Delta E^*(\Delta K_{11}^*)$ . These calculated values of  $\beta_1^*$  and  $\beta_2^*$  then provide another

approximation for the next value of  $K_{ii}^*$ ,  $K_{ii}^*(3)$ , as

$$K_{ii}^*(3) = K_{ii}^*(2) + K_{ii}^*(2) (2 \Delta \beta^* - \beta_2^*) / (\beta_2^* - \beta_1^*), \quad (58)$$

$\beta^*$  and  $\Delta E^*$  are again calculated for  $K_{ii}^*$  given by equation (58), denoted by  $\beta_3^*$  and  $\Delta E_3^*$  respectively. The following values of  $K_{ii}^*$  are then quadratically extrapolated from these values of  $\beta_1^*$ ,  $\beta_2^*$  and  $\beta_3^*$  which are renewed in a bootstrap fashion to continue the routine until the maximum number of table entries plus five is reached. Such a procedure is equivalent to employing a three point Lagrange interpolation formula on the known set of points

$\{x_i, f_i = f(x_i)\}$  for  $i = 1, 2, 3$  where  $x$ 's are the  $K_{ii}^*$ 's and  $f$  is the function  $\Delta E^*$ . Then the function  $f$  evaluated at a point  $x$  is (Abramowitz and Stegun, 1968)

$$f(x) = \sum_{j=1}^3 l_j(x) f_j, \quad (59)$$

where

$$l_j(x) = \prod_{\substack{i=1 \\ i \neq j}}^3 \frac{(x - x_i)}{(x_j - x_i)}. \quad (60)$$

Usually,  $x$  is known and equations (59) - (60) give the interpolated value of the function at  $x$ ,  $f(x)$ , from the known values of  $x_j$  and  $f_j$  for  $j = 1, 2, 3$ . Here,  $f(x)$  is taken as the required  $\beta^*$ ,  $\beta^*(i) = i \Delta \beta^*$  and  $x$  is to be calculated as the solution of equation (59). Reintroducing  $K_{ii}^*(i) = x_i$  and  $\beta^*(i) = f_i = i \Delta \beta^*$ ,  $K_{ii}^*(i+3)$  can be determined from  $K_{ii}^*(i)$ ,  $K_{ii}^*(i+1)$ ,  $K_{ii}^*(i+2)$  and their associated temperatures  $\beta^*(i)$ ,  $\beta^*(i+1)$ ,  $\beta^*(i+2)$  from the expression:

$$K_{ii}^*(i+3) = (-b + \sqrt{b^2 - 4a(c - \beta^*(i+3))}) / 2a. \quad (61)$$

where

$$a = \sum_j g(j)$$

$$b = \sum_j \sum_{\substack{k \\ j \neq k}} g(j) K_{ij}^*(k)$$

$$c = \sum_j g(j) \prod_{k \neq j} K_{ij}^*(k)$$

where

$$g(j) = \beta^*(j) / \prod_{l \neq j} (K_{ij}^*(j) K_{ij}^*(l)) .$$

The limits on the summations and products are  $i$  to  $i + 2$ .

The above approach gives a table of  $\Delta E^*$  values at an approximate  $\beta^*$  grid size of  $\Delta \beta^*$ , usually taken as

$$\Delta \beta^* = \beta^* / N_p , \quad (62)$$

where  $N_p + 5$  is the number of entries in the table and  $\beta^*$  is the reciprocal temperature being considered. In the subsequent calculations  $N_p = 32$ , resulting in a thirty-seven entry table for  $\Delta E^*$  which is then to be used to obtain  $\Delta A^*$  via Gaussian quadrature. The additional five entries allow possible interpolation about  $\beta^*$  to be made inside the table without recourse to further unwarranted extrapolations. It will be shown in Appendix 7 that the value of the dipolar contribution to the internal energy at  $\beta^*$ ,  $\Delta E^*(\beta^*)$ , plays an important role in calculating the Gibbs free energy of the mixture. Thus, the importance given to the accurate determination of  $\Delta E^*(\beta^*)$  from interpolation on the table of  $\Delta E^*$  values.

The actual values of  $\beta^*$  required to perform the quadrature on  $\Delta E^*$  are rescaled to the domain  $[-1, 1]$  by the transformation described beneath equation (55). The weights  $w_i$  and abscissas  $x_i$  for the Gaussian quadrature were taken from the tables of Abramowitz and Stegun (1968) correct to the eighth decimal place for  $m = 4, 8, 16$  and  $32$ . Such data were stored using the subroutine Gauss ( $m, a, w$ ), which, when the value of  $m$  was passed from another subroutine, returned the abscissas  $a(i)$  and weights  $w(i)$  as arrays of dimension  $m/2$ . Table 1 gives the effect of increasing  $m$  on the value of the integral of  $\Delta E^*$  over  $0$  to  $\beta^*$ . It is seen that if the values of  $\Delta E^*$  at the abscissas are given by a six point interpolation formula, then such values are correct to at least one or two digits in the sixth decimal place. The error in the numerical integration of  $\Delta E^*$  over these points is dependent on the value of  $m$ . For  $m = 4$ , the error is at most  $.02\%$  for  $\beta^* = 3.7$  and less than  $.003\%$  at other  $\beta^*$ , in general. This error is significantly diminished for the  $m = 8$  quadrature where the integration can be considered accurate to at least one or two digits in the sixth decimal place, i.e. the percentage error is of the order of  $10^{-3} \%$ . Thus the dipolar contributions to the internal energy, Helmholtz free energy and pressure of a mixture of dipolar hard spheres should be accurately determined to one or two digits in the sixth decimal place.

#### 4.4 Calculation of Dipolar Contribution to the Pressure

The dipolar contribution to the pressure,  $\Delta P$ , can then be determined from the difference of  $\Delta E/V$  and  $\Delta A/V$  (Adelman and Deutch, 1973; Sutherland et al., 1974). Multiplying equation (18) by

$\pi R_1^6/48m_1^2$  gives the dipolar contribution to the pressure in reduced units,  $\Delta P^*$ , where

$$\Delta P^* = \Delta E^* - \Delta A^* , \quad (63)$$

noting that  $\Delta E^*$  and  $\Delta A^*$  are defined as volume densities in equation (23). In the single component case Sutherland et al. (1974) have shown graphically how  $\Delta P^*$  is sufficiently negative to induce van der Waals loops into otherwise monotonically decreasing isotherms of a hard sphere reference system as the reduced volume ( $\sim \rho^{*-1}$ ) increases. For constant composition mixtures, these van der Waals loops are found in the total pressure,  $P^* = P_0^* + \Delta P^*$ , of a mixture as the total reduced number density decreases. The occurrence of these loops is dependent on the temperature as for the pure component example above. However, the detailed temperature and composition dependencies of the pressure of a dipolar mixture are only an intermediate in the calculation of the phase behaviour for a binary system, and so only the qualitative findings will be summarized.

At any given  $P^*$ ,  $\beta^*$  and  $x$ , there are either one or three values of  $\rho^*$  which satisfy the equation of state  $P^* = P^*(\rho^*, \beta^*, x)$ . For the mixture case, the effect of composition changes on the value of  $\rho^*$  which is given from inversion of the equation of state at any fixed values of  $P^*$  and  $\beta^*$  will now be considered. Since we are essentially interested in the liquid-liquid phase part of the general phase diagram (points in  $P, T, x$  space), the greatest  $\rho^*$  value will be selected, for the case of pure component one, which has the smaller polarity of the two dipolar hard spheres. It was found that as the more polar constituent, species two, was added to the mixture ( $x$  increased), the isotherm was shifted to higher values

of  $\rho^*$ . This was indicative of the physical picture of the stronger attractive forces of the more polar species contracting the mixture to allow more particles within the fixed volume of the container. Given the solution  $\rho^*$  at  $x = 0$  for a given  $P^*$ , the effect of increasing  $x$  at constant  $P^*$  was to increase  $\rho^*$ . Thus if the pure component one was found to have a density  $\rho^*$  characteristic of a liquid,  $\rho^* \gtrsim .01$  for a pure dipolar hard sphere fluid, this liquid property at a given  $P^*$  and  $\beta^*$  would be enhanced as  $x$  increased to unity. Fortunately, a rescaling of the vapour pressure curve of the pure fluid (Sutherland et al., 1974) allowed choices of  $P^*$  and  $\beta^*$  to be made which gave  $\rho^*$  on the liquid region of a polynomial fit to the vapour pressure curve. Thus, the above method of solving for the density at a given pressure as composition changes is equivalent to the fundamental problem of checking each of the three (one) zeros of  $P^*(\rho^*)$ , calculating the associated free energy, and finally selecting the root which minimized the free energy. An additional check on the correctness of the value of  $\rho^*$  was given through the positiveness of the compressibility at that point. If the slope of  $P^*$  at that  $\rho^*$  were positive, the solution was thermodynamically unstable and rejected. The liquid and unstable densities were closer to each other than either was to the metastable gaseous root for these values of  $\beta^*$  and  $P^*$  constrained to the fluid ( $\beta^* < \beta_c^*$ ) and liquid ( $\beta^* > \beta_c^*$ ) regimes where  $\beta_c^* = 4.444$  is the inverse reduced critical temperature. In other words, the composition variable has the same effect as decreasing temperature on a single component system, and, in so doing, achieves the same result of increasing the liquid character of the system for a given  $P^*$  and  $\beta^*$ .

#### 4.5 Calculation of Excess Properties

In summary, the above search routine for the  $K_{\alpha\beta}$  allows the dipolar contributions to the internal energy density, Helmholtz free energy density and the pressure to be calculated once  $\rho^*$ ,  $x$  and  $\beta^*$  are initialized. Further, the Mean Spherical Approximation allows the dipolar contributions to the Gibbs free energy density to be obtained directly from  $\Delta E^*$ . The details of this equality are given in Appendix 7. These values are calculated in a Fortran subroutine, PMIX, which embodies the tabulation of  $\Delta E^*$  at approximately equal intervals of  $\beta^*$ ,  $\Delta \beta^*$ , subsequent interpolation of the table to perform the Gaussian quadrature which is then used to calculate  $\Delta A^*$ . For the particular value of  $\beta^*$ , a further interpolation gives  $\Delta E^*(\beta^*)$  which on subtracting from  $\Delta A^*$  gives the dipolar pressure,  $\Delta P^*$ . The total pressure of the mixture, PMIX, is  $\Delta P^*$  plus the pressure contribution from the hard spheres at the same density and composition. This latter term is calculated from the compressibility factor given by the Mansoori-Carnahan-Starling-Leland equation for mixtures of hard spheres. This and other reference state properties are calculated in the subroutine called STATE, at the same values of  $\rho^*$  and  $x$  specifying the density and composition of the dipolar mixture. The basic quantity calculated is GMIXT which is the Gibbs free energy of the dipolar mixture in excess of an ideal gas mixture at the same composition,  $x$ , pressure, PMIX, and temperature,  $\beta^*$ . GMIXT is given, in units of  $NkT$ , by

$$GMIXT = \frac{8\beta^* \Delta G^*}{\frac{\pi}{6} \rho R_1^3} + \frac{G_o^{ex}}{NkT}, \quad (64)$$

where  $G_o^{ex} = G_o^{ex}(N_1, N_2, PMIX, T)$  of equation (14).

GMIXT can then be used to obtain the Gibbs free energy of the dipolar mixture in excess of the unmixed ideal gas free energies, GMIX, a quantity used by van Konynenburg (1968) in his studies of the phase diagrams for van der Waals mixtures. From equation (12), it follows that GMIX is given by

$$GMIX = GMIXT + GIDEAL \quad , \quad (65)$$

where

$$GIDEAL = \sum_{\alpha=1}^2 x_{\alpha} \ln x_{\alpha} .$$

The " $x \ln x$ " term is the ideal term for changes in the free energy on mixing ideal components, in this case ideal gas components which arise in the definitions of the excess properties used in this thesis. For ideal gas mixtures and ideal mixtures in general,  $GMIXT = 0$  and equation (65) reduces to the ideal entropic " $x \ln x$ " term. This behaviour was used to further test the program for equal radii-equal dipole moments. It was found that the use of a six point interpolation scheme coupled to a thirty two point table gave GMIX correctly to at least the fifth decimal place. The tolerance used for the calculated pressure,  $PMIX$ , being in agreement with the fixed value of the pressure,  $PMIX1$ , was cautiously taken to be  $10^{-8}$ . For values of  $\rho^*$  such that  $|PMIX(\rho^*) - PMIX1| < 10^{-8}$ , the value of  $GMIXT$  at the particular convergent value of  $\rho^*$  was calculated and, in turn, GMIX was obtained for the overall mole fraction, temperature and pressure,  $PMIX1$ , being considered.

The more important use of GMIX, however, was that it, rather than GMIXT, can be used in a common tangent construction to obtain the details of coexisting phase compositions if phase separation does occur. An equally appropriate function for this criterion is the Gibbs free energy of mixing, GXS. This is obtained through the calculation of the Gibbs free energy of the pure components, one and two, at the same pressure and temperature of the mixture. Denoting this function by GPURE, it is defined and used to calculate GXS in equations (66) and (67), respectively:

$$G_{\text{PURE}} = \sum_{\alpha} x_{\alpha} G_{\alpha, \text{pure}}(P_{\text{MIX}}, T) . \quad (66)$$

$$\begin{aligned} G_{\text{XS}} &= G_{\text{MIXT}} + G_{\text{IDEAL}} - G_{\text{PURE}} \\ &= G_{\text{MIX}} - G_{\text{PURE}} . \end{aligned} \quad (67)$$

In equation (66),  $G_{\alpha, \text{pure}}(p, T)$  is the Gibbs free energy of the  $\alpha^{\text{th}}$  pure component minus the kinetic energy contribution (ideal gas term, given by  $\ln \Lambda_{\alpha}^3$ ) at pressure  $p = P_{\text{MIX}}$  and temperature  $T$ .  $G_{\alpha, \text{pure}}(p, T)$  is calculated from the single component equations (Sutherland et al., 1974; Rushbrooke et al., 1973), and is in units of  $NkT$ .  $G_{1, \text{pure}}(p, T)$  also serves as a subsidiary check on the accuracy of the numerical procedures to calculate GMIXT at zero mole fraction for all values of pressure and temperature. It so happens that GPURE is essentially the equation of the straight line joining the endpoints  $(x=0, G_{1, \text{pure}})$  and  $(x=1, G_{2, \text{pure}})$  of the plot in  $(x, G_{\text{MIX}})$  space. This is seen readily from rewriting equation (66) as

$$G_{\text{PURE}} = (G_{2, \text{pure}} - G_{1, \text{pure}})x + G_{1, \text{pure}} .$$

Thus, GXS vanishes at the endpoints  $x = 0, 1$  of the composition plot  $(x, GXS)$ . The advantage of using the latter composition plot rather than  $(x, GMIX)$  is that the curvature of the  $(x, GMIX)$  plot is heavily masked by GMIX's near linearity in  $x$ . However, the subtraction of this linear behaviour, as given in the definition of GXS, completely removes this difficulty and allows a significant improvement in the construction of a common tangent between any suitable points along a  $(x, GXS)$  plot. Since the stability (or instability) of any mixture is defined in terms of the positivity (or negativity) of  $(\partial^2 G / \partial x^2)_{p,T}$  where  $G$  is the total Gibbs free energy of the mixture, it follows from the linear dependence of the ideal gas contribution of each species (equation (12)) and GPURE on  $x$  that the regions of (in)stability are identical to  $G$ , GMIX and GXS. However, the case of convenient application of the common tangent construction to specify regions of coexisting phases increases in that order. A further excess Gibbs free energy,  $G^E$ , the excess of GXS over the ideal gas mixture contribution GIDEAL, was not considered since the common tangent construction was not as directly applicable as it is to GXS. In this notation,  $G^E$  is given as

$$\begin{aligned} G^E &= GXS - GIDEAL \\ &= GMIXT - GPURE \end{aligned} \quad (68)$$

For completeness,  $G^E$  has been defined above since it could be obtained from the results GMIXT and GPURE if any comparison with other calculations involving  $G^E$  for dipolar hard sphere mixtures were required. These unfortunately have not been done using other techniques such as perturbation theories and Monte Carlo calculations. Appendix 8 gives the formal definitions of the excess free energies employed here.

#### 4.6 Computer Programs and Details

This Section is a composite of the actual listings of the subroutines of the program (physically presented as Appendix 9) and their operation. In order to facilitate handling of input data and output files, the program was set up on disc to be entered sequentially from Batch mode in RT 11. Each execution of such a program gave twenty-six triads (x, GMIX, GXS) which were for a given  $T = \text{TEMP}$  and  $P = \text{PMIX1}$  for fixed values of the ratios  $m_2/m_1 = XM$  and  $R_2/R_1 = W$ . These sets of triads, along with the values of  $XM$ ,  $W$ ,  $\text{TEMP}$  and  $\text{PMIX1}$ , were stored on disc as unformatted data files to be processed for common tangency of points (x, GXS) later after the complete batch run had ended. A typical batch job had eighty-one runs to execute and could be interrupted and restarted at the point of (un)intentional stoppage. After the batch job had finished the data on disc was backed-up on magnetic tape and a separate listing of the job statistics (time and data) taken and that file deleted from disc. The batch job also initiated the setting-up of the eighty-one data files needed to initialize values of parameters required in each run. Such information is symbolized in the data file:

W, XM, RHO

M, NINTRP, NPTS

PMIX1

TEMP

where RHO is the initial value of  $\prod_6 K_{11} \rho_1 R_1^3$  to be used in the calculation of GPURE,  $M = 8$  is the order of the Gaussian quadrature,  $\text{NINTRP} = 6$  is the order of interpolation formula to obtain  $\Delta A^*$  from a table of  $\text{NPTS} = 32 (+ 5)$  entries of  $\Delta E^*$  values. RHO is not to be confused with  $\rho$  or  $\rho^*$  introduced earlier.

These data files were automatically read under BATCH by the Fortran program, SAMPRO, which consisted of a main of the same name and thirteen other Fortran subroutine or function subroutine programs. The purpose of SAMPRO was to calculate GXS, GMIX for  $x = 0$  to 1 modulo .04 at the given TEMP and PMIX1 values. An additional output file gave a listing of the values of convergent  $\pi \rho R_1^3 / 6$ , GMIX, GXS, and the difference in the pressure which satisfied the  $10^{-8}$  tolerance criterion for these pressures, PMIX1 and PMIX ( $\rho^*$ ), being equal. These list files were initially stored on disc, listed and then deleted. PMIX1 was taken as  $n/2$  multiples of the critical pressure for pure component one,  $P_c^* = .000461$  and  $n = 1, \dots, 11$ . For each PMIX1, TEMP could be varied according to the areas of interest in the phase diagram. However the grid spacing for the temperature became apparent only after the experience of many runs. The grid size ranged from .001, .005, .010, to .020. At each temperature and pressure point, the generation of the (x, GMIX, GXS) arrays varied in time according to the size of W. For  $W = 1$ , the average time was approximately ten minutes on the PDP 11/45; as W varied from unity by  $\pm .01$ , this time could be up to a factor of three longer. Thus, a batch job covering three values of PMIX1, in each of which twenty-seven values of TEMP ranged from .16 to .50, could take at least fourteen hours of computer time for equal radii calculations and forty-two hours for nonequal radii calculations. These lengthy calculations were found for  $W = 1 \pm .01$  and the time factor alone thus prohibited any larger deviation from the equal radii case being undertaken, although more realistic deviations, say 5-10%, were certainly considered, but only partially done because of enormous time factor involved. Appendix 10 contains a sample of the listed

output for  $W = .99, 1.0, 1.01$  at constant values of  $XM = 1.5$ . Rather than give a detailed analysis of the qualitative trends in GXS and GMIX as a function of  $x$ , TEMP and PMIX1, since these trends are used to obtain a constant pressure projection of  $(P, T, x)$  space, the details of the common tangent construction will be presented in the following Section.

## 5. Common Tangent Construction

It is well recognized (Prigogine and Defay, 1973; Rowlinson, 1971) that the existence of regions of immiscibility in binary mixtures can be induced from violations of the stability criterion for mixtures viz., for stability of a mixture at the specified  $T$ ,  $p$  and  $x$ ,  $(\partial^2 G / \partial x^2)_{p,T} > 0$ . For values of  $T$  and  $p$  for which this criterion is satisfied for all compositions  $x$ , the components are miscible in all proportions. In such a case, the composition plot of the Gibbs free energy of the mixture versus composition,  $x$ , is convex downwards. As  $T$  and  $p$  change, immiscibility between components may occur and this is associated with the geometrical phenomenon of a local maximum appearing in the composition plot, at which point  $(\partial^2 G / \partial x^2)_{T,p} < 0$ . Such qualitative information in the form of the violation of a stability criterion on the sign of  $(\partial^2 G / \partial x^2)_{T,p}$  only gives the fact that the system is unstable at  $p$  and  $T$  for the composition range in which the local maximum occurs in  $G$ . The regimes of instabilities are interpreted to be the formation of nonhomogeneity in the single phase system, i.e., a phase separation has taken place providing two or more phases in equilibrium at a lower free energy than single phase system would have at the same  $p$  and  $T$ .

The compositions of the two phases in equilibrium are  $x'$  and  $x''$  where ' and '' distinguish the phases.  $x'$  and  $x''$  can be obtained from a geometrical construction on the composition plot of the Gibbs free energy of the mixture (in units of  $NkT$ ) known as the common tangent construction (Rowlinson, 1971; Prigogine and Defay, 1973). From equality of the chemical potentials of each species in the co-existing phases, it can be shown that not only are the slopes of the points  $x'$  and  $x''$  equal but also there exists a common tangent of the same slope between  $x'$  and  $x''$  which describes the variation in the Gibbs free energy of the phases intermediate in composition ( $x'$ ,  $x''$ ). These are summarized in the equalities (Prigogine and Defay, 1973)

$$\left(\frac{\partial g'}{\partial x'}\right)_{T,p} = \left(\frac{\partial g''}{\partial x''}\right)_{T,p} \quad (69)$$

and

$$g' - g'' = \left(\frac{\partial g'}{\partial x'}\right)_{T,p} (x' - x'') \quad (70)$$

where  $g'$  ( $g''$ ) is the Gibbs free energy of the ' (') phase per molecule, and  $(\partial g' / \partial x')_{T,p}$  is taken as the slope of the common tangent construction. Equation (70) is used to identify the compositions  $x'$  and  $x''$  of the phases which are coexisting, by locating compositions along the Gibbs free energy plot which have the same slope  $(\partial G / \partial x)_{T,p}$  and are joined by a tangent of the same slope. The tangent necessarily replaces the convex-upward region of the composition plot of the Gibbs free energy with the lower Gibbs free energy of the phase separated system, geometrically given in equation (70). While the thermodynamic equalities employed in obtaining equations (69) and (70) are exact, the practical application of locating the mole fractions  $x'$  and  $x''$  according to the common tangent construction is cumbersome and liable to large errors.

A computer program COMTAN was written to minimize the error and improve the practicability of the method. Large errors ( $\sim 20\%$ ) are necessarily involved in the selection and drawing by hand of the tangent between any two points on a graph which are deemed to satisfy equations (69) and (70). The program essentially calculated the numerical derivative of GXS with respect to  $x$  from a five point Lagrange differentiation formula (Abramowitz and Stegun, 1968) and found the compositions for which the differences of the slopes and the slope of the chord joining those points were a minimum. The data output file containing the twenty-six triads ( $x$ , GMIX, GXS) with  $\Delta x = .04$  was employed as a table on which a seven point Lagrange interpolation formula was used to refine the  $x$  grid size to  $\Delta x = .01$ . This gave GXS (or GMIX) as a one hundred dimensional array, the  $(4n+1)^{th}$  entry of which was the original calculation for mole fraction  $x = n/25$ ,  $0 \leq n \leq 25$ .

The actual analysis of the common tangent construction was not fully automated and required the user to examine the composition plot as depicted on a GT 40 screen via Quickplot. A domain of  $x$  values (more precisely, the integral representation of  $x = n \Delta x$ ) was chosen and the program returned those points, within that range, at which the slopes of the adjoining chord and of the tangents at each point were the closest in value. The search for the coexisting mole fractions with the same slope as the adjoining chord was cleverly initialized to commence at least  $\ell - \Delta x$  units apart. This additional constraint prohibited the search from returning  $x$ 's whose slopes were nearly equal and yet whose adjoining chord was above other points in the composition plot.

The above search routine for points of common slope as the adjoining straight line gave the values of the coexisting compositions,  $x'$  and  $x''$ , to within  $\pm .01$  mole fraction units. However this was quite satisfactory as any points  $x'$  and  $x''$  for a given TEMP and PMIX1 which were considered doubtful were re-evaluated with  $\Delta x = .005$  and these new values for the compositions used in the T-x diagram. In order to check that the results for the collection of T-x coordinates for a fixed pressure were adequate from the  $\Delta x = .01$  grid, the runs were redone with  $\Delta x = .005$ . Fortunately, the quantitative characteristics of the temperature-composition graph were unchanged to within physical limits of the graphical presentation.

Greater difficulty was encountered with the critical points (both liquid-liquid and liquid-gas types). The flattening of the coexistence region in the vicinity of the critical point of the mixture disadvantaged the program with the choice of many points whose slopes were nearly identical. A reduction in the temperature grid size about these critical points provided new files which were analyzed by COMTAN. However it was found that the critical point could only be approached asymptotically with the  $\pm .01$  error and not accurately determined within any smaller  $\Delta x$  grid size. This is particularly disappointing in view of the van der Waals mixture studies of Scott and van Konynenburg (1968) which gave critical line data to the fourth decimal place. However the van der Waals mixture equations are much simpler, the worst computation being the order of the solution of a cubic polynomial for its zeros. With these comments concerning the critical point data in mind, the results and diagrams of the temperature composition data are examined

in the next Chapter with the emphasis on the role played by the molecular parameters in the phase equilibria of dipolar hard sphere mixtures.

## Chapter 4

### Results and Conclusions

#### 1. Composition Plots of the Gibbs Free Energy

This Chapter presents the results of the calculations of the change in the Gibbs free energy of mixing at constant pressure,  $P^*$ , and temperature,  $T^*$ . As indicated in Chapter 3, this information takes the form of a table of twenty-six entries of values of  $GXS$ , the  $i^{\text{th}}$  entry being the change in free energy of mixing for the composition of the mixture given by mole fraction  $x_i = (i-1)/25$ . Each table is calculated for specified values of  $P^*$  and  $T^*$ , which assume the values  $P^* = .001383, .001613, .001844, .002074$  and  $T^* = .16, .17, .18, \dots, .50$ . The range of values for  $P^*$  and  $T^*$  chosen here are only a subset of the data files actually calculated. However, the choice of  $P^*$  values allows considerable information to be obtained about the effects of molecular properties on the extent of phase equilibria in a binary mixture of dipolar hard spheres.

Since the composition plots of the Gibbs free energies are an intermediate step in the calculation of the temperature composition curve, only a few remarks will be given concerning their general characteristics. For regions in  $(P^*, T^*)$  space where the components mix in all proportions (i.e. all values of  $x$ ,  $0 \leq x \leq 1$ ),  $GXS$  is concave upward everywhere. Depending on  $(P^*, T^*)$ , the temperature can be raised or lowered until a point  $(P^*, T^{*'})$  is reached at which  $GXS$  assumes over a certain composition range a concave downward curvature. This behaviour geometrically "mimics" phase separation at  $(P^*, T^{*'})$ , and

can be used in the thermodynamic argument of the common tangent construction to obtain the compositions of the coexisting phases, say,  $x'$  and  $x''$ . The collection of the  $T^*$  dependence of pairs  $(x', x'')$  describing the composition of phases in equilibrium at the same pressure  $P^*$  is the temperature-composition plot. For mixtures of dipolar hard spheres, local maxima were generally found at values of  $(P^*, T^*)$  in the ranges considered above, and for a ratio of the dipole moments fixed at 1.5. Such frequent occurrence of immiscibilities was expected since rough estimates from the work of van Konynenburg (1968) showed comparable trends for the conditions of  $(P^*, T^*)$  and the type of systems considered here. For  $T^* \sim .16$ , liquid-liquid immiscibility was found consistently for all molecular systems mentioned above (see Figures 2-25). This immiscibility of the polar components was identified by the appearance of local maxima in GXS. The minimal value of GXS was found to be shifted to higher values of  $x$  as  $T^*$  increased (compare Figures 2 and 5). In other words, mixing was enhanced for a mixture containing larger amounts of the more polar component, rather than for mixtures of intermediate compositions, where  $x \sim .5$ . Such asymmetry in the GXS curve is a consequence of the deviations of the polar mixture from ideality, where GXS would be symmetrical about  $x = .5$  and given by GIDEAL defined for equation (65) of Chapter 3.

At these low temperatures ( $T^* \sim .16$ ) the geometrical properties of GXS imposed a negative gradient on the common tangent (Figures 2, 6, 10, 14, 18 and 22). As the temperature increased at fixed pressure, entropy contributions to the Gibbs free energy of the mixture became important. This was reflected primarily in the

displacement of the asymmetrical minimum from regions of high  $x$  values to low compositions,  $x \lesssim .5$ . This is seen in the sets of Figures: 2-5, 6-9, 10-13, 14-17, 18-21 and 22-25. The actual details of such a transition are complicated in terms of GXS and its curvature properties as a function of  $T^*$ ,  $P^*$  and the molecular parameters identifying the components. Fortunately, the detailed information is more clearly explained in terms of the effects  $P^*$  and the molecular parameters have on the temperature-composition curves. The discussion will be postponed until the following Section, which gives such details. However, the change in the curvature of GXS can be summarized in terms of the change in slope of the common tangent, when it is defined for coexisting phases. As  $T^*$  changes, the slope of the common tangent undergoes a change in sign, becoming more positive as the temperature increases (e.g., Figures 2-5). This change in slope was directly associated with the movement of the asymmetrical minimum in GXS to lower values of  $x$  as the temperature increased.

Figures 2-25 are a collection of the representatives of the composition plot of GXS for the three values of the ratio of the diameters,  $w$ , with  $w = .99, 1.00, 1.01$ . Four temperatures in the vicinity of  $T^* = .18, .28, .38$  and  $.48$  were chosen for each value of  $w$ . Only two pressures were considered,  $P^* = .001383$  and  $P^* = .002074$ , the minimum and maximum pressures for which the temperature-composition curves were studied. Although only twenty-six points are given in the composition plots of GXS, one, two or five hundred such points (obtained through interpolations of the original table of twenty-six entries) are used in the common tangent construction. These plots were drawn on the HP 9830 Graphics unit

from data points transferred on ASC II papertape from the PDP 11/45 computer. The data were formatted as truncated to the fourth decimal place, i.e., F 7.4 format specification was used. The timescale for each such plot was limited by the time taken up in the manual operations involved, viz., setting up of the Graphics unit each time and the actual reading of the papertape. Each plot for twenty-six data points was typically one to two minutes in preparation time (aside from labelling and numeration of the axes which was done by hand).

## 2. Temperature-Composition Plots in Phase Diagrams

The temperature-composition ( $T^*$ ,  $x$ ) plots are given in Figures 26-28. These  $T^*$ - $x$  diagrams are given for fixed values of  $P^*$ . By varying  $P^*$ , one can obtain the locus of points ( $P^*$ ,  $T^*$ ,  $x$ ) where the coordinates ( $T^*$ ,  $x$ ) are obtained from the temperature-composition diagram appropriate for the value of  $P^*$ . The totality of ( $P^*$ ,  $T^*$ ,  $x$ ) coordinates is known as the phase diagram of the binary system under consideration. From the choice of ( $T^*$ ,  $x$ ) for each  $P^*$  value, it follows that the boundaries in ( $P^*$ ,  $T^*$ ,  $x$ ) space separate regions of miscibility and immiscibility of components. This and other elementary properties of phase diagrams are well-known to physical chemists (Prigogine and Defay, 1973; Rowlinson, 1971; Castellan, 1972). Clearly the amount of computer time taken to generate a large number of ( $P^*$ ,  $T^*$ ,  $x$ ) coordinates prohibits the calculation of any detailed phase diagram. However, the general characteristics of the phase diagram can be partially given by the pressure dependence of the  $T^*$ - $x$  diagrams. An examination of the pressure dependence of the shape of the  $T^*$ - $x$  diagrams can then be studied in turn as a function of the molecular differences in the

species composing the mixture. Such an approach would provide specific details of the effects of the molecular interactions (given in terms of the associated potential parameters) on the phase diagram of the binary system for the pressures considered. Fortunately, the qualitative information of the  $T^*-x$  diagrams calculated here for a mixture of dipolar hard spheres is so strikingly similar to the corresponding curves of van Konynenburg (1968) that the general characteristics of the phase diagrams are approximately the same as those of van Konynenburg (Scott, 1975). Although no quantitative comparison is made, the above correspondence is certainly reconciled through the basic similarity of the intermolecular potentials of the two approaches.

In this thesis, the intermolecular potential is the dipole-dipole interaction as described by equation (3) of Chapter 2. The properties of mixtures of particles, interacting through the dipole potential plus a short-range hard core repulsion, are summarized in Figures 26-28. Figures 26-28 are the  $T^*-x$  plots for  $w = 1.01, 1.00, .99$  all of which are taken at the same fixed ratio of  $m_2/m_1 = 1.5$ . The corresponding relative polarities are given by the ratios  $(\beta m_2^2/R_2^3) / (\beta m_1^2/R_1^3) = 2.25/w^3$  (polarity of a molecule being measured by  $\beta m^2/R^3$ , after Rowlinson (1971)). As  $w$  decreases, the ratio of the polarities increase roughly by about three percent. For  $w = 1.01, 1.00, .99$ ,  $2.25/w^3$  is found to be 2.18, 2.25, and 2.32. However, such small changes in the polarities of the second component have a significant effect on the characteristics of the  $T^*-x$  diagrams.

Similar behaviour has been found for mixtures whose pressure is described by the van der Waals equation:

$$p = \frac{RT}{\tilde{V} - b} - \frac{a}{\tilde{V}^2} . \quad (1)$$

In equation (1),  $R$  is the universal gas constant and the composition properties of the mixture are given in the composition dependence of the van der Waals constants  $a$ ,  $b$  (van Konynenburg, 1968). The parameters  $a$  and  $b$  are defined in:

$$a = \sum_{i,j} x_i x_j a_{ij} , \quad (2)$$

and

$$b = \sum_{i,j} x_i x_j b_{ij} , \quad (3)$$

where  $a_{ij}$  ( $b_{ij}$ ) are the parameters appropriate for the  $i$ - $j$  species attractive (repulsive) interaction. The mixing rules (consistent with the choice of molecular parameters describing the unlike-species interaction as required in the solution of the Mean Spherical Approximation for dipolar mixtures) are the so-called geometric mean law for the  $a_{12}$  parameter and the additivity of diameters for the  $b_{12}$  parameter. These are given by equations (4) and (5):

$$a_{12} = \sqrt{a_{11} a_{22}} , \quad (4)$$

and

$$b_{12} = ((b_{11}^{1/3} + b_{22}^{1/3})/2)^3 . \quad (5)$$

The effects of deviations in  $a_{12}$  from the form of equation (4) on phase behaviour for mixtures obeying van der Waals equation of state have been intensively studied by van Konynenburg. A wide variety of different behaviour is possible for different

mixing rules governing the behaviour of  $a_{12}$ . However for values of

$a_{12}$  given by equation (4) three types of different phase diagrams are found (Types II, III<sub>m</sub> and III in van Konynenburg's notation for the equal diameter case). The ratio of the polarities of the species for van der Waals mixtures is determined by  $(a_{22}b_{11})/(a_{11}b_{22})$ .

In deriving the analogue of  $(m_1^2 R_1^3)/(m_2^2 R_2^3)$ , the following basic interpretation of the parameters  $a_{ij}$  and  $b_{ij}$  in terms of modern potential characteristics is used (Scott and van Konynenburg, 1970).

The parameter  $a_{ij}$  is related to  $\epsilon_{ij} R_{ij}^3$ , where  $\epsilon_{ij}$  is the well depth of the potential energy function for the i-j interaction and

$R_{ij}$  the associated collision diameter. For dipolar mixtures, it then follows that  $a_{ij} \sim \epsilon_{ij} R_{ij}^3 \sim m_i m_j$ , and so the polarity as measured by  $\beta m_\alpha^2 / R_\alpha^3$  is proportional to  $a_{\alpha\alpha}$  for each species  $\alpha$ .

The average value of  $a_{22}/a_{11}$  values connected with mixture properties classified as Type III<sub>m</sub> is 1.76, approximately. A relative increase (decrease) of about four percent in  $a_{22}/a_{11} = 1.76$  is sufficient to cause a change in Type III<sub>m</sub> behaviour to Type III (Type II) behaviour (van Konynenburg, 1968). Assuming that the weak attractive tail of the potential associated with the van der Waals isotherm (Isihara, 1971) could be described by dipolar forces, the correspondence is given that  $a_{ij} \sim m_i m_j$ . Thus the corresponding values of  $m_2^2/m_1^2 = 1.76$  (van der Waals) and  $m_2^2/m_1^2 = 2.25$  (Mean Spherical Approximation) give qualitatively similar T\*-x curves for the equal diameter case,  $b_{11}=b_{22}$  and  $w = 1$ , respectively.

For the equal diameter case, this similarity of the T\*-x curves of van Konynenburg and of this thesis (Figure 27) would indicate that the dipolar properties of the mixture are under-estimated by the approximations of the Mean Spherical Approximation.

However, changes in the ratio of the polarity of the species forming

the mixture do have the same effect in the two models. In the work of van Konynenburg, the small change in polarity was accomplished through variation of the attractive parameters ( $a_{ij}$ 's) keeping the repulsive parameters ( $b_{ij}$ 's) fixed at equal values. In contrast to this approach, we have considered the effects of equivalent changes in the ratio of the polarities through small changes in the diameter of molecules of species two. If the molecular size of component two is decreased, its effective polarity is increased. Such an increase in the polarity of the molecules of species two (with respect to that of molecular species one) causes further dissimilarity in the molecular properties of each species than was the case for species of the same molecular size. The consequences of this increase in dissimilarities of species are seen in Figure 28. There is an overall growth of the regions of immiscibility of the two components for all temperatures and pressures. Only for high  $P^*(\sim 2.074 \times 10^{-3})$  and moderate  $T^*(\geq .45)$  is there evidence of a liquid-gas critical temperature. The critical locus of this temperature moves to higher values of  $x$  as the pressure decreases. There is no evidence of the lower critical solution temperature for the liquid-gas transition at  $T^* \sim .25-.35$ . Due to the relatively large differences in the molecular properties of the species, very high pressures,  $P^* \gg 5 \times 0.00461$ , are required to guarantee mixing at intermediate temperatures of the order of  $T^* \sim .30$ . As the temperature falls below  $T^* \sim .20$ , there is no evidence of a liquid-liquid upper critical solution temperature. These features are also found in the classification of van Konynenburg under Type III. It should be expected that decreasing  $w$  from  $w = .99$  to values of  $w \sim .5$  could increase the regions of immiscibility at low

temperatures even more. In that case, immiscibility of species could also occur at high  $T^*$  and high  $P^*$  values ( $T^* > 1$ ,  $P^* > 50 \times .000461$ ). This phenomenon has been described as fluid-fluid immiscibility (Rowlinson, 1971; van Konynenburg, 1968; Neff and McQuarrie, 1975).

The effect of increasing pressure on the regions of immiscibility in Figure 28 is not sufficiently strong to allow the formation of a homogeneous liquid phase at all values of  $x$ . However, for species of equal diameters (thus differing in dipole moment only), these same regions of  $T^*-x$  space are ones of miscibility. This is seen in Figure 27, where the ratio of polarities of the species is 2.25. At the same  $P^*$  values considered in Figure 28, the regions of immiscibility have dramatically decreased with the sectioning of the  $T^*-x$  plots of Figure 28 into a liquid-vapour equilibrium "wing-shaped" part and a liquid-liquid equilibrium "dome-shaped" part. At pressures above  $P^* = .002074$ , there is no liquid-vapour immiscibility but only immiscibility between liquid phases below  $T_c^* \sim .186$ . On the other hand, the lower pressure dependence ( $P^* = .001383$ ) of the  $T^*-x$  diagram is almost Type III in character. It should be noticed that at  $T^* = .22$  the coexisting phases on the  $P^* = .001383$  curve are very close in comparison to their values at the same conditions for the molecular system in Figure 28. Indeed, for this particular component system of equally-sized particles, the effect of increasing the pressure is very significant. This is seen in the  $P^* = .001613$  curve. Here, the existence of a homogeneous liquid mixture is evidenced (at that pressure) in the temperature range  $.206 < T^* < .27$ . At this particular pressure (and higher pressures also), there are three critical temperatures: two upper

critical solution temperatures (liquid liquid:  $T_c^* = .207$  ; liquid-gas:  $T_c^* = .458$  ) and one lower critical solution temperature (liquid-gas:  $T_c^* = .268$  ). In the liquid-liquid dome, the liquid-liquid critical temperature decreases slowly and the associated critical composition is fairly constant ( $x_c \sim .35$ ) for increases in the pressure. It follows that the amount of liquid-liquid immiscibility is not significantly reduced by pressure increases.

However, the liquid-vapour immiscibility regions are far more sensitive to pressure increases as expected with the presence of a vapour phase. As pressure is increased from  $P^* = .001613$  to  $.002074$ , the lower critical solution temperature readily increases and the critical composition is fairly constant. In contrast, although the upper critical solution temperature (liquid-gas) is decreased by roughly the same amounts as the lower critical solution temperature, the critical composition is very sensitive to pressure increases, moving to lower  $x$  values quite dramatically. The combined effect is to considerably reduce the liquid-gas immiscibility region until at  $P^* = .002535$  there is complete miscibility at all compositions above the liquid-liquid critical temperature,  $T_c^* \sim .185$  . These characteristics of the  $T^*-x$  diagrams displayed in Figure 27 are readily found in the  $T^*-x$  diagrams for van der Waals mixtures which are classified Type III<sub>m</sub> in van Konynenburg's thesis. For equal radii, the ratio of the square of the dipole moments directly measures the ratio of the polarity of the components, viz.,  $m_1^2/m_2^2 = 2.25$  for  $w = 1$ . In comparison with the earlier case of  $m_1^2 R_1^3 / m_2^2 R_2^3 = 2.32$  for  $w = .99$ , this is a three percent relative decrease in the ratio of the polarities of the components. This increase in the similarity of

components two and one (as measured by the polarity,  $\beta m^2/R^3$ ) is quite significant and leads to larger regions of miscibility in the  $T^*-x$  diagram.

The details of the effects on the  $T^*-x$  diagram of a further 3% relative decrease in the polarity of species two are given in Figure 26. Here the diameter of the hard core of component two is 1.01 larger than that of component 1. From  $w = 1.01$  and  $m_2^2/m_1^2 = 2.25$ , it follows that the ratio of the polarity of species two to species one is 2.18. From Figure 26, the  $T^*-x$  diagram for  $P^* = .001383$  has the separate liquid-vapour and liquid-liquid immiscibility regions. For the  $w = 1.00$  case, such features appeared at higher  $P^*$  values,

$P^* \geq .001613$ . The gain in similarity of the molecular properties of the species is reflected in the onset of miscibility at much lower pressures than was found with mixtures containing more dissimilar molecular species. Liquid-liquid immiscibility is found at considerably lower temperatures, again a phenomenon attributable to the closeness of the molecular polarity of the components. For  $P^* = .001383$ , single phase liquid mixtures are found at all compositions over the range of temperatures  $.16 \leq T^* \leq .28$ . The effect of larger pressures on this system is to decrease the amount of liquid-liquid equilibrium until such immiscibility is not found to occur even at  $T^* = .15$  for  $P^* = .001613$ . A corresponding decrease also takes place in the regions of liquid-vapour equilibria. Such a decrease in the immiscibility of phases for intermediate temperatures continues until the fluid phases become miscible in all proportions for  $P^* \geq .002074$ . In particular, if  $P^* = .002074$  and  $.002535$ , it was found that the components mixed freely for all values of  $x$

over the temperature range  $0.15 < T^* < 0.50$ . Such features of the  $T^*-x$  diagrams in Figure (26) are found to be very similar to the van der Waals mixtures properties as classified by van Konynenburg as Type II. This Section then completes the presentation and discussion of the results.

### 3. Conclusions

The results of a model calculation for the mixing properties of dipolar hard spheres have been presented above. A clear interpretation has been given for the influence of the molecular parameters  $m_1, R_1, m_2, R_2$  on the overall features of phase behaviour of three molecularly similar systems.

The properties of the mixture of dipolar hard spheres are partitioned into a hard sphere contribution and a dipolar term in excess of the hard sphere term. In evaluation of the hard sphere contribution to the thermodynamic properties of the dipolar mixture, the thermodynamic formalism (Hill, 1954; Prigogine and Defay, 1973) has been calculated from the hard sphere mixture results of Baxter (1970). Baxter's compressibility pressure is employed to give an accurate representation of the hard sphere contribution to the thermodynamic functions using the suggestions of Mansoori et al. (1971). Supplementary to these hard sphere thermodynamic functions, the dipolar contribution to the pressure and Gibbs free energy are calculated through the solution of the Mean Spherical Approximation for mixtures of dipolar hard spheres. It should be pointed out that the thesis divides naturally into two parts: the solution of the Mean Spherical Approximation for mixtures of dipolar hard spheres, and

an application of the associated thermodynamic functions of these dipolar mixtures to the study of molecular properties and their effects on phase behaviour.

The first part of the problem involved the solution of the Mean Spherical Approximation for dipolar mixtures. It was shown in Chapter 2 how Wertheim's technique for the simpler problem of the solution of the Ornstein-Zernike equation for a pure fluid of dipolar hard spheres can be extended successfully to the general multicomponent case. An important step in the final solution of the binary mixture case is the use of Baxter's factorized form of an Ornstein-Zernike-like equation (Baxter, 1970). This allows the self-consistency equations for the  $K_{\alpha\beta}$ 's to be correctly formulated, and so the problem of the binary mixture case to be completed once these self-consistent equations have been solved for the  $K_{\alpha\beta}$ . As seen in Chapter 2, the distribution functions  $h_{\alpha\beta}(r_1, \Omega_1, r_2, \Omega_2)$  are determined, albeit in a rather complicated manner, from knowledge of the  $K_{\alpha\beta}$ . The investigation of these molecular distribution functions is currently in progress by the author. Since such detailed information as contained in the  $h_{\alpha\beta}$ 's is not required in the calculation of the thermodynamic properties of the system, the  $K_{\alpha\beta}$ 's were used to calculate the dipolar contributions to the pressure, internal energy, Helmholtz and Gibbs free energies of the dipolar mixture.

A successful application of these thermodynamic properties of the dipolar hard sphere mixture has been given for the quantitative effects of the molecular interactions on the phase behaviour of selected mixtures. It is evident that a combination of parameters describing these interactions is utilized rather than individual selections of parameters separately. From Chapter 2, the solution of the self-consistent equations for  $K_{\alpha\beta}$  required the combinations  $\beta m_1^2 \rho_1$  and  $\beta m_2^2 \rho_2$ . These parameters measure the total reduced dipole moment per unit volume of the container. Introduction of reduced variables defined the reduced inverse temperature  $\beta^* = \beta m_1^2 / R_1^3$  which is also identified as a measure of the polarity of a molecule of species one (Rowlinson, 1971). Thus the polarity of species  $\alpha$  arises quite naturally in the treatment of a mixture of dipolar hard spheres via the Mean Spherical Approximation.

As the polarity of the second component increases relative to the fixed polarity of component one, it was found above that the increase in dissimilarity of the two species incurred further regions of immiscibility in the relevant  $T^*-x$  diagram. Originally, it was thought by the author that dipolar forces might not be sufficiently strong to induce phase separation in a system. The model of dipolar hard spheres allowed the existence of any phase separation to be directly attributable to the presence of the dipole interaction. Such a conclusion was based on the evidence (Alder, 1964; Lebowitz and Rowlinson, 1964) that mixtures of hard spheres do not show any indication of a phase separation. The results of this thesis show that even though the dipole interaction is non-directional (in the

sense that it angle-averages to zero) and weak compared to dispersion forces etc., it is possible to observe a multitude of phase equilibria between the dipolar hard spheres of each species in the mixture.

Qualitative agreement is given with the calculations of van Konynenburg (1968) provided the relative changes in the polarities of the species are used when such a comparison of the  $T^*-x$  diagrams is made. It is relevant to mention here that regions of immiscibility of dipolar hard spheres do not exist for the mixture defined by  $w = 1$ ,  $m_2/m_1 = 1.1, 1.2, 1.3$  and  $1.4$ . This initial investigation was confined to the ranges  $.10 < T^* < .50$  and  $P^* = .000692, .000922, .001153, .001383, .001613, .001814, .002074$  and  $.002535$ .

## Chapter 5

### Future Research

There are several interesting areas of research which ought to be investigated further.

1. A more intensive study of the complete phase diagram should be carried out with a view to locating three-phase lines and azeotropic behaviour. In making further comparisons with the behaviour of van der Waals mixtures, the  $a_{\alpha\alpha}$  and  $b_{\alpha\alpha}$  should be fitted to the liquid-gas critical parameters as given by Høye et al. (1974).
  
2. Before making any quantitative predictions concerning real experimental trends, the inadequacies of the Mean Spherical Approximation should be corrected through use of the Generalized Mean Spherical Approximation of Høye et al. (1974). This procedure would essentially involve the fitting of several adjustable parameters defined in the Yukawa correction term. The set of parameters is then adjusted to the critical points of the pure components for which experimental data of mixing properties are available.
  
3. The deviations of the mixing rule from the geometric mean have been used to explain high pressure behaviour of the fluid-fluid critical line. This was possible through the lessening of the unlike-species' interaction and was developed for a mixture of particles interacting via a Lennard-Jones potential (Neff and McQuarrie, 1975). For a dipolar mixture, the interaction between molecules of unlike species could analogously be modulated as  $\xi m_1 m_2$ .

Although this adjustment of the dipolar interaction is not rigorously justified, the solution of the Mean Spherical Model can still be carried through in a straightforward way. In this way, the effect of deviations from the geometric mean can be introduced and its influence on the phase diagrams can be obtained.

4. An increase in the dissimilarity of the molecular species of the mixture should allow high pressure-high temperature immiscibility regions to be found in the  $T^*-x$  diagrams. Such regions of fluid-fluid immiscibility could be examined from the approach of Neff and McQuarrie (1975).

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Table 1

The effects of different interpolation (NINTRP = 3, 4, 5, 6, 7, 8, 9, 10) and quadrature (M = 4, 8) schemes are calculated for a table of  $(\beta^*(j), -\Delta A^*(j), \Delta E^*(j), \Delta P^*(j))$  values. Here  $\beta^*(j) = j/10$ , where  $j = 1, 2, \dots, 39$ . The values of  $K_{11}^*(j)$  are selected from DI = .005 and N = 40 (see text in Chapter 3, Section 4.3). The choice of NINTRP = 6 and M = 8 for the generation of the  $\Delta E^*$  table gives excellent agreement with those values of  $\Delta A^*$ ,  $\Delta E^*$  and  $\Delta P^*$  calculated from the formulae of Rushbrooke et al. (1973).

4POINT QUAD      6POINTS FOR INTERP GIVEN      40

[illegible]

150



8POINT QUAD 8POINTS FOR INTERP GIVEN 40				8POINT QUAD 8POINTS FOR INTERP GIVEN 40				8POINT QUAD 8POINTS FOR INTERP GIVEN 40			
1	0.005702	-0.011112	-0.005410	2	0.010836	-0.020573	-0.009737	3	0.015462	-0.028644	-0.013182
4	0.019646	-0.035590	-0.015944	5	0.023453	-0.041636	-0.018183	6	0.026936	-0.046958	-0.020022
7	0.030141	-0.051692	-0.021551	8	0.033105	-0.055941	-0.022836	9	0.035859	-0.059786	-0.023927
10	0.038430	-0.063293	-0.024863	11	0.040838	-0.066510	-0.025671	12	0.043103	-0.069478	-0.026375
13	0.045239	-0.072231	-0.026992	14	0.047260	-0.074794	-0.027535	15	0.049176	-0.077192	-0.028016
16	0.050998	-0.079442	-0.028444	17	0.052734	-0.081561	-0.028827	18	0.054392	-0.083562	-0.029170
19	0.055977	-0.085456	-0.029479	20	0.057497	-0.087255	-0.029758	21	0.058955	-0.088965	-0.030010
22	0.060356	-0.090596	-0.030239	23	0.061705	-0.092153	-0.030448	24	0.063005	-0.093642	-0.030637
25	0.064259	-0.095070	-0.030811	26	0.065471	-0.096440	-0.030969	27	0.066642	-0.097756	-0.031114
28	0.067776	-0.099023	-0.031247	29	0.068875	-0.100244	-0.031369	30	0.069940	-0.101422	-0.031481
31	0.070974	-0.102559	-0.031585	32	0.071979	-0.103658	-0.031679	33	0.072955	-0.104722	-0.031767
34	0.073904	-0.105752	-0.031847	35	0.074828	-0.106750	-0.031922	36	0.075729	-0.107719	-0.031990
37	0.076606	-0.108659	-0.032053	38	0.077462	-0.109572	-0.032111	39	0.078296	-0.110461	-0.032165
8POINT QUAD 8POINTS FOR INTERP GIVEN 40				8POINT QUAD 8POINTS FOR INTERP GIVEN 40				8POINT QUAD 8POINTS FOR INTERP GIVEN 40			
1	0.005702	-0.011112	-0.005410	2	0.010836	-0.020573	-0.009737	3	0.015462	-0.028644	-0.013182
4	0.019646	-0.035590	-0.015944	5	0.023453	-0.041636	-0.018183	6	0.026936	-0.046958	-0.020022
7	0.030141	-0.051692	-0.021551	8	0.033105	-0.055941	-0.022836	9	0.035859	-0.059786	-0.023927
10	0.038430	-0.063293	-0.024863	11	0.040838	-0.066510	-0.025671	12	0.043103	-0.069478	-0.026375
13	0.045239	-0.072231	-0.026992	14	0.047260	-0.074794	-0.027535	15	0.049176	-0.077192	-0.028016
16	0.050998	-0.079442	-0.028444	17	0.052734	-0.081561	-0.028827	18	0.054392	-0.083562	-0.029170
19	0.055977	-0.085456	-0.029479	20	0.057497	-0.087255	-0.029758	21	0.058955	-0.088965	-0.030010
22	0.060356	-0.090596	-0.030239	23	0.061705	-0.092153	-0.030448	24	0.063005	-0.093642	-0.030637
25	0.064259	-0.095070	-0.030811	26	0.065471	-0.096440	-0.030969	27	0.066642	-0.097756	-0.031114
28	0.067776	-0.099023	-0.031247	29	0.068875	-0.100244	-0.031369	30	0.069940	-0.101422	-0.031481
31	0.070974	-0.102559	-0.031585	32	0.071979	-0.103658	-0.031680	33	0.072955	-0.104722	-0.031767
34	0.073904	-0.105752	-0.031847	35	0.074829	-0.106750	-0.031921	36	0.075729	-0.107719	-0.031990
37	0.076606	-0.108659	-0.032053	38	0.077462	-0.109573	-0.032111	39	0.078296	-0.110461	-0.032165
8POINT QUAD 10POINTS FOR INTERP GIVEN 40				8POINT QUAD 10POINTS FOR INTERP GIVEN 40				8POINT QUAD 10POINTS FOR INTERP GIVEN 40			
1	0.005702	-0.011112	-0.005410	2	0.010836	-0.020573	-0.009737	3	0.015462	-0.028644	-0.013182
4	0.019646	-0.035590	-0.015944	5	0.023453	-0.041636	-0.018183	6	0.026936	-0.046958	-0.020022
7	0.030141	-0.051692	-0.021551	8	0.033105	-0.055941	-0.022836	9	0.035859	-0.059786	-0.023927
10	0.038430	-0.063293	-0.024863	11	0.040838	-0.066510	-0.025671	12	0.043103	-0.069478	-0.026375
13	0.045239	-0.072231	-0.026992	14	0.047260	-0.074794	-0.027535	15	0.049176	-0.077192	-0.028016
16	0.050998	-0.079442	-0.028444	17	0.052734	-0.081561	-0.028827	18	0.054392	-0.083562	-0.029170
19	0.055977	-0.085456	-0.029479	20	0.057497	-0.087255	-0.029758	21	0.058955	-0.088965	-0.030010
22	0.060356	-0.090596	-0.030239	23	0.061705	-0.092153	-0.030448	24	0.063005	-0.093642	-0.030637
25	0.064259	-0.095070	-0.030811	26	0.065471	-0.096440	-0.030969	27	0.066642	-0.097756	-0.031114
28	0.067776	-0.099023	-0.031247	29	0.068875	-0.100244	-0.031369	30	0.069940	-0.101422	-0.031481
31	0.070974	-0.102559	-0.031584	32	0.071979	-0.103658	-0.031679	33	0.072955	-0.104722	-0.031767
34	0.073904	-0.105752	-0.031847	35	0.074828	-0.106750	-0.031922	36	0.075729	-0.107719	-0.031990
37	0.076606	-0.108659	-0.032053	38	0.077462	-0.109572	-0.032111	39	0.078296	-0.110461	-0.032165

Figure 1

The radial distribution function  $g(r)$  for a spherically symmetric potential.

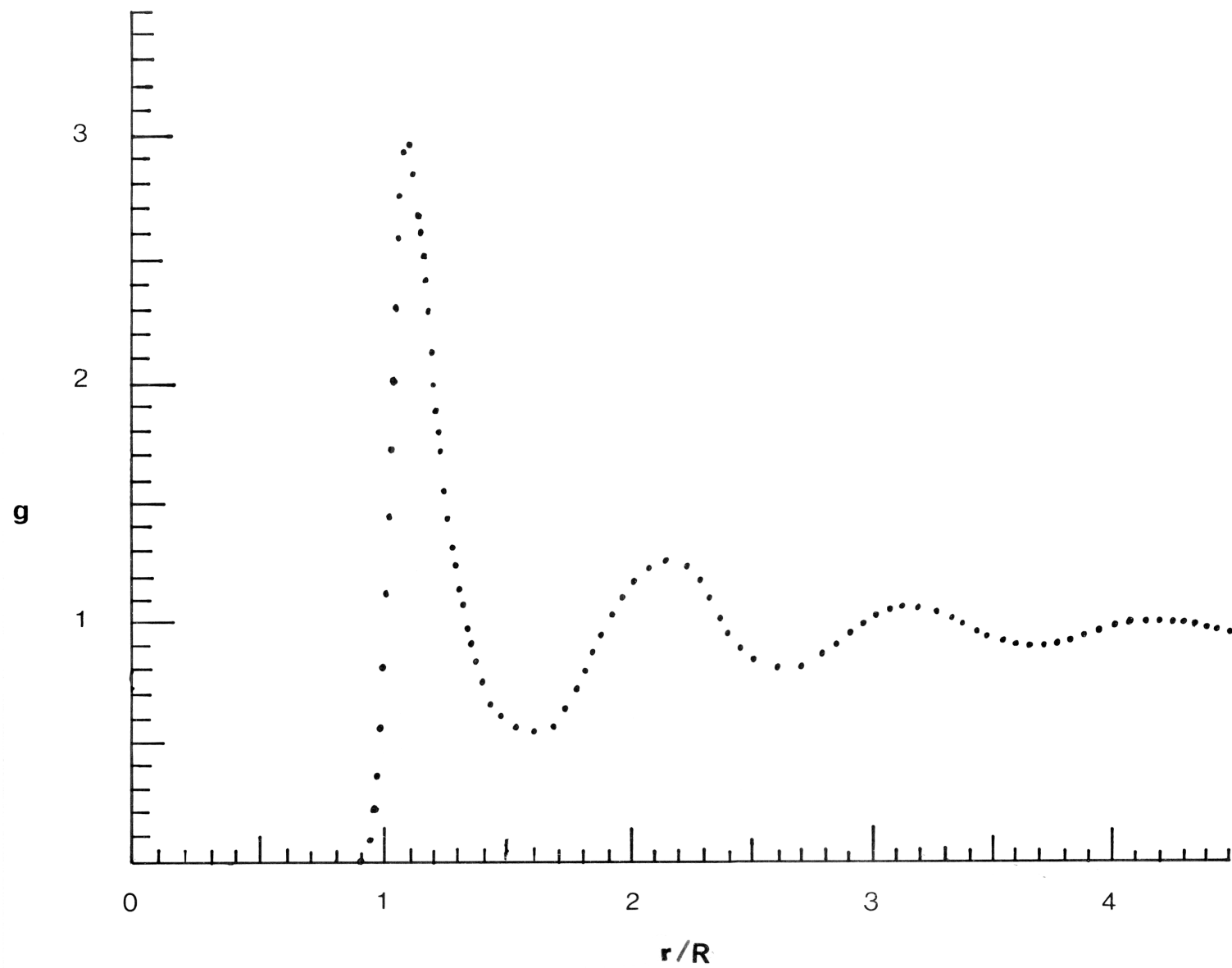


Figure 2

The composition plot of the Gibbs free energy for  $T^* = .18$ ,  
 $P^* = .001383$ ,  $W = .99$ ,  $GMIN = -.17$ . GXS is given in units of  
GMIN.

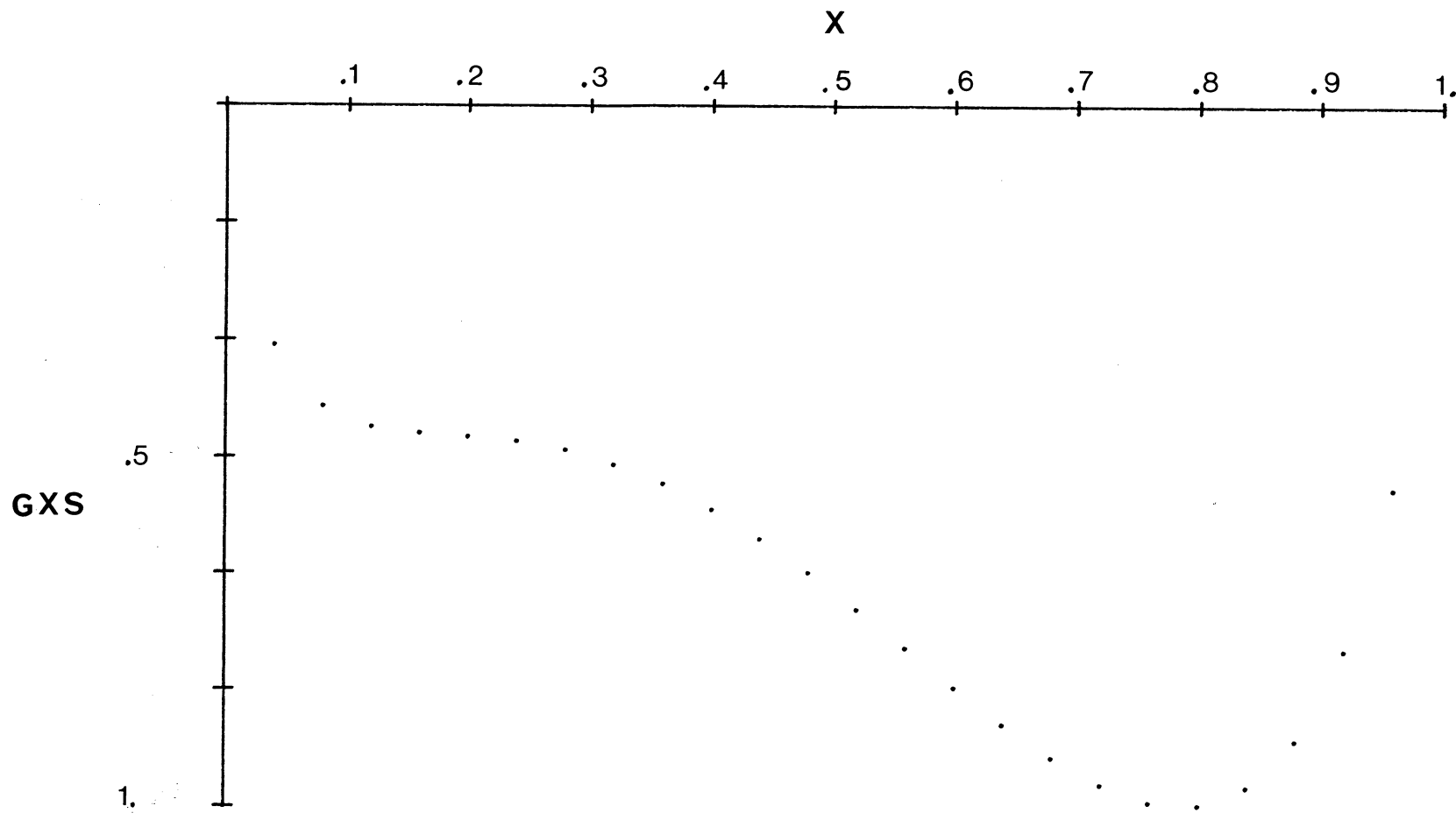


Figure 3

The composition plot of the Gibbs free energy for  $T^* = .28$ ,  
 $P^* = .001383$ ,  $W = .99$ ,  $GMIN = -.21$ . GXS is given in units of  
GMIN.

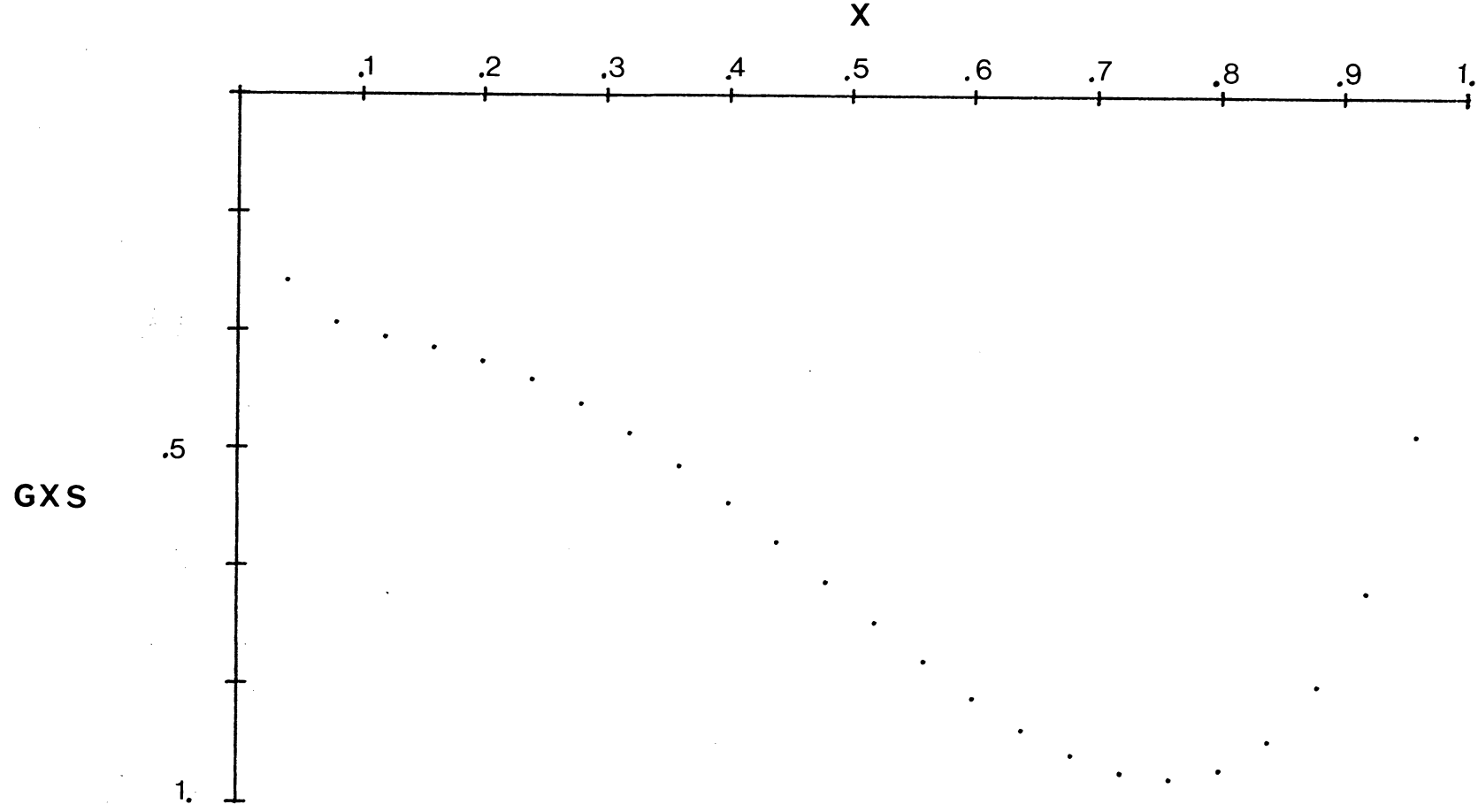


Figure 4

The composition plot of the Gibbs free energy for  $T^* = .38$ ,  
 $P^* = .001383$ ,  $W = .99$ ,  $GMIN = -.20$ . GXS is given in units of  
GMIN.

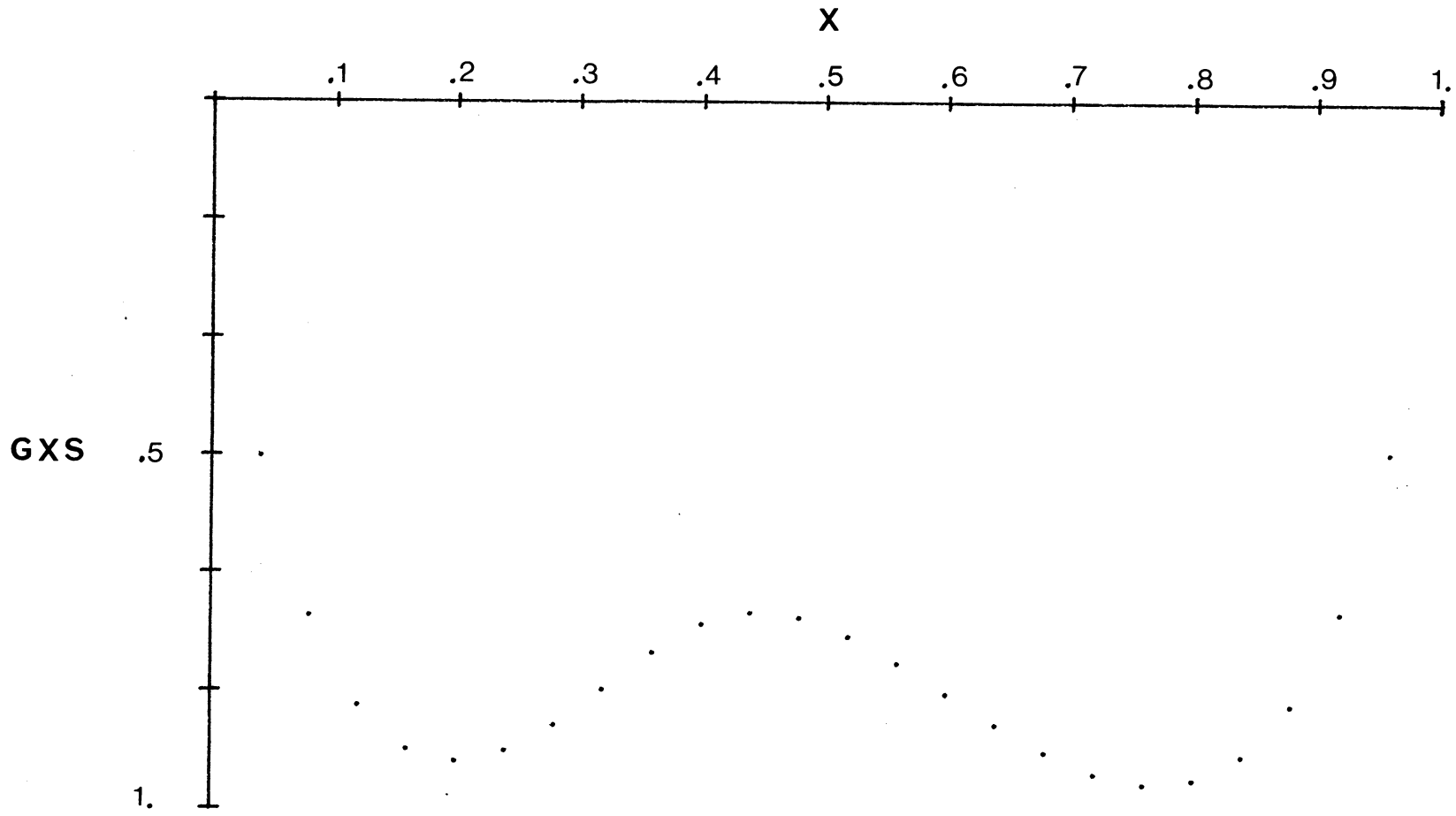


Figure 5

The composition plot of the Gibbs free energy for  $T^* = .48$ ,  
 $P^* = .001383$ ,  $W = .99$ ,  $GMIN = -.47$ . GXS is given in units of  
GMIN.

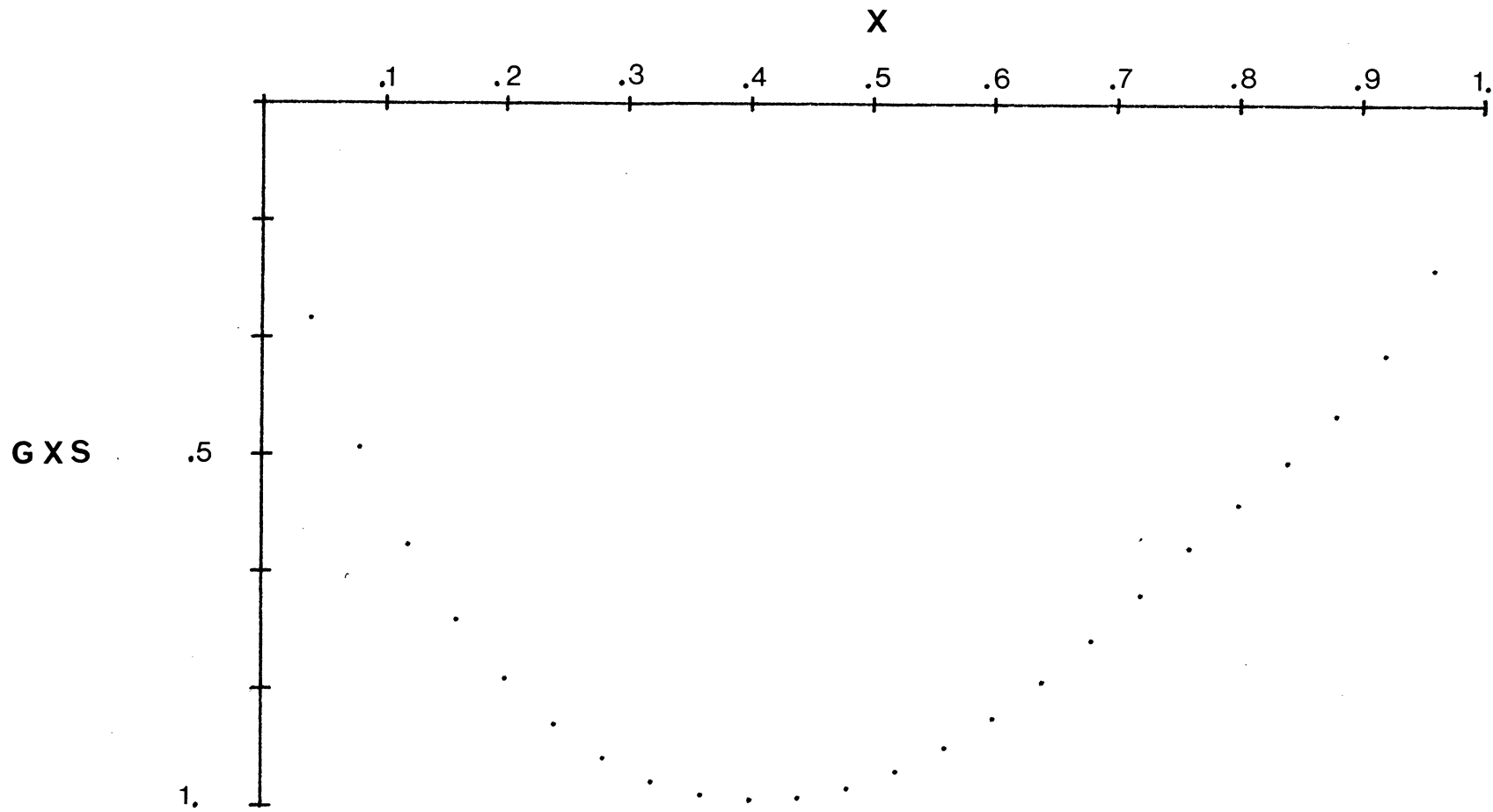


Figure 6

The composition plot of the Gibbs free energy for  $T^* = .18$ ,  
 $P^* = .002074$ ,  $W = .99$ ,  $GMIN = -.18$ . GXS is given in units of  
GMIN.

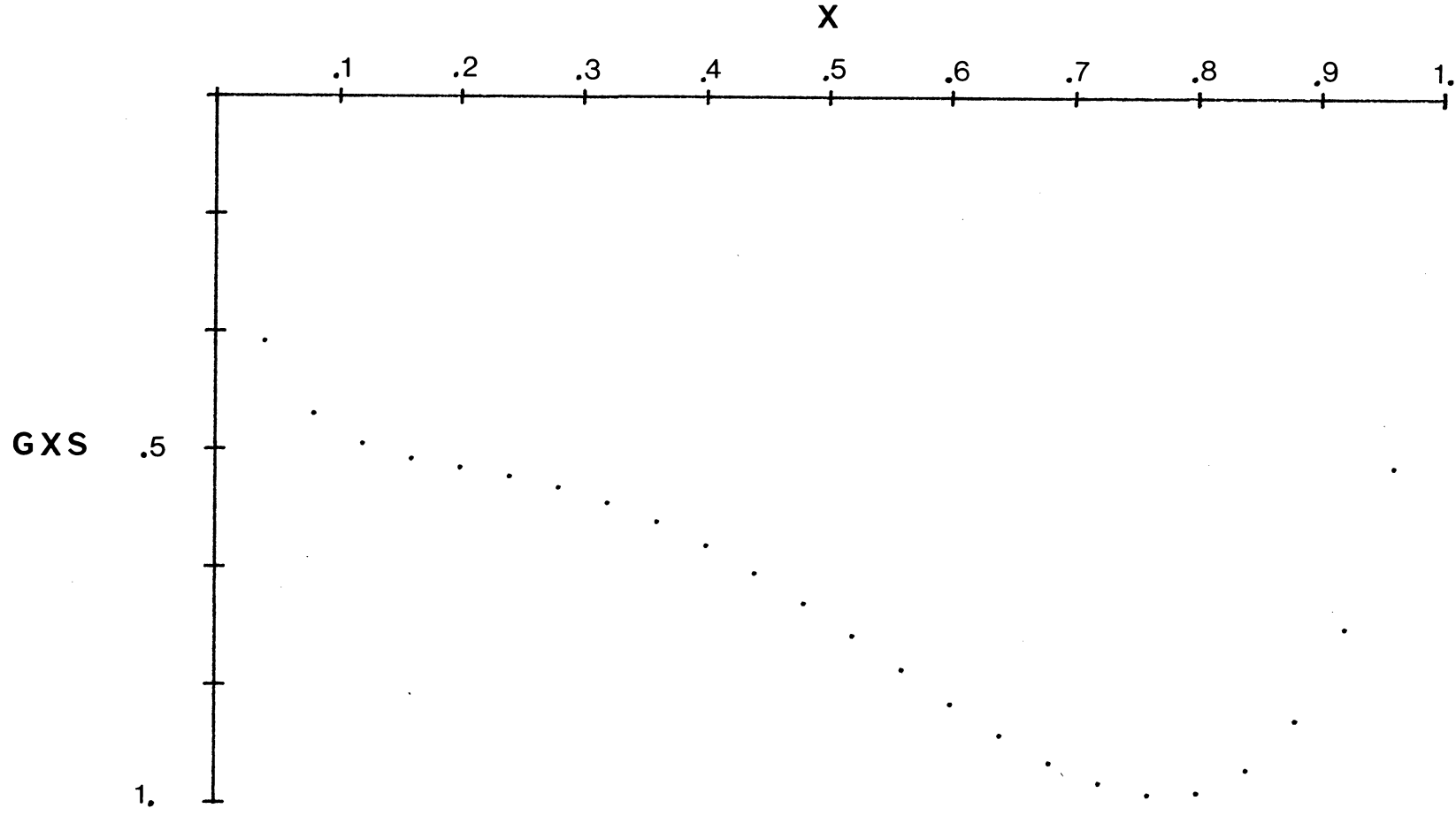


Figure 7

The composition plot of the Gibbs free energy for  $T^* = .27$ ,  
 $P^* = .002074$ ,  $W = .99$ ,  $GMIN = -.24$ . GXS is given in units of  
GMIN.

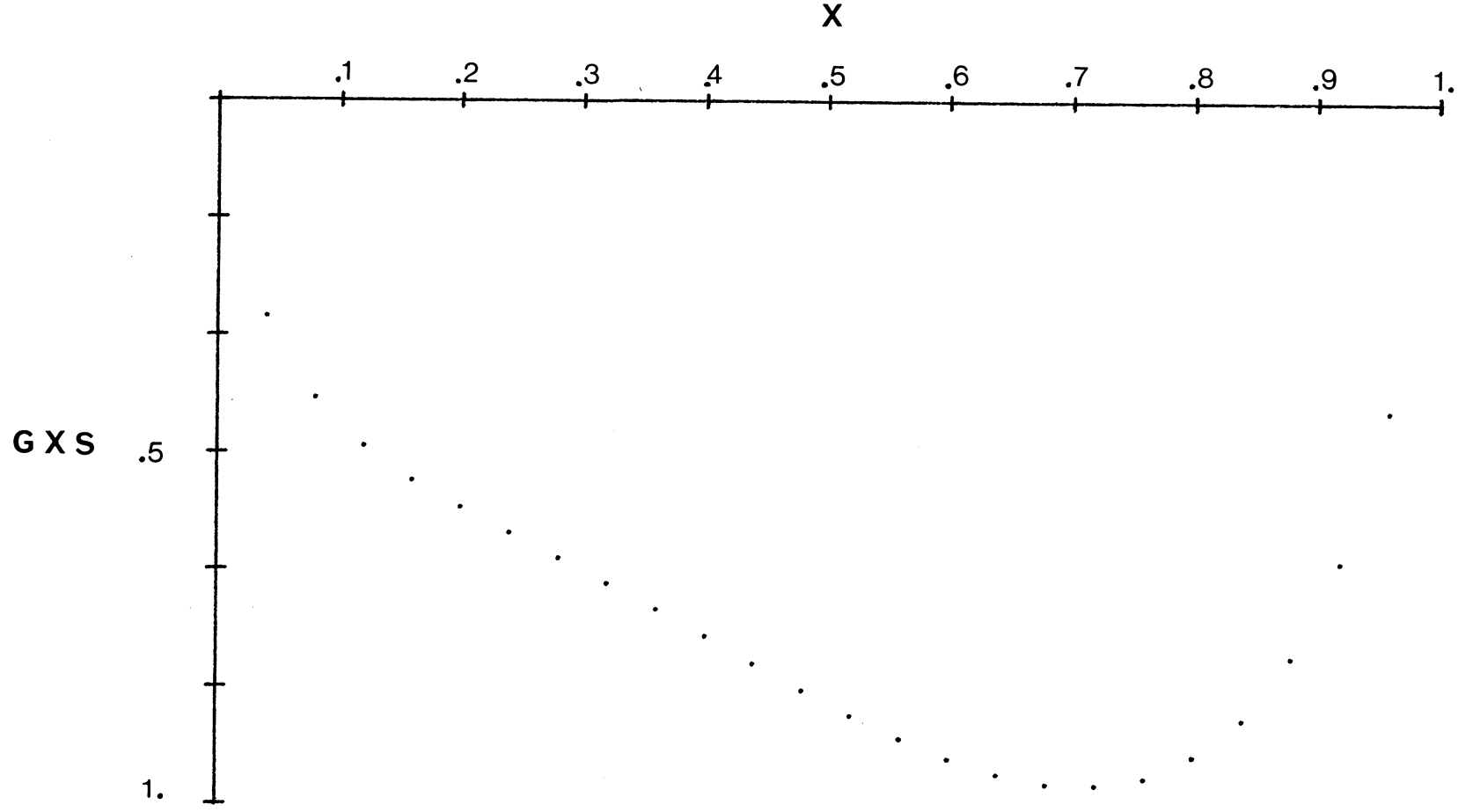


Figure 8

The composition plot of the Gibbs free energy for  $T^* = .38$ ,  
 $P^* = .002074$ ,  $W = .99$ ,  $GMIN = -.26$ . GXS is given in units of  
GMIN.

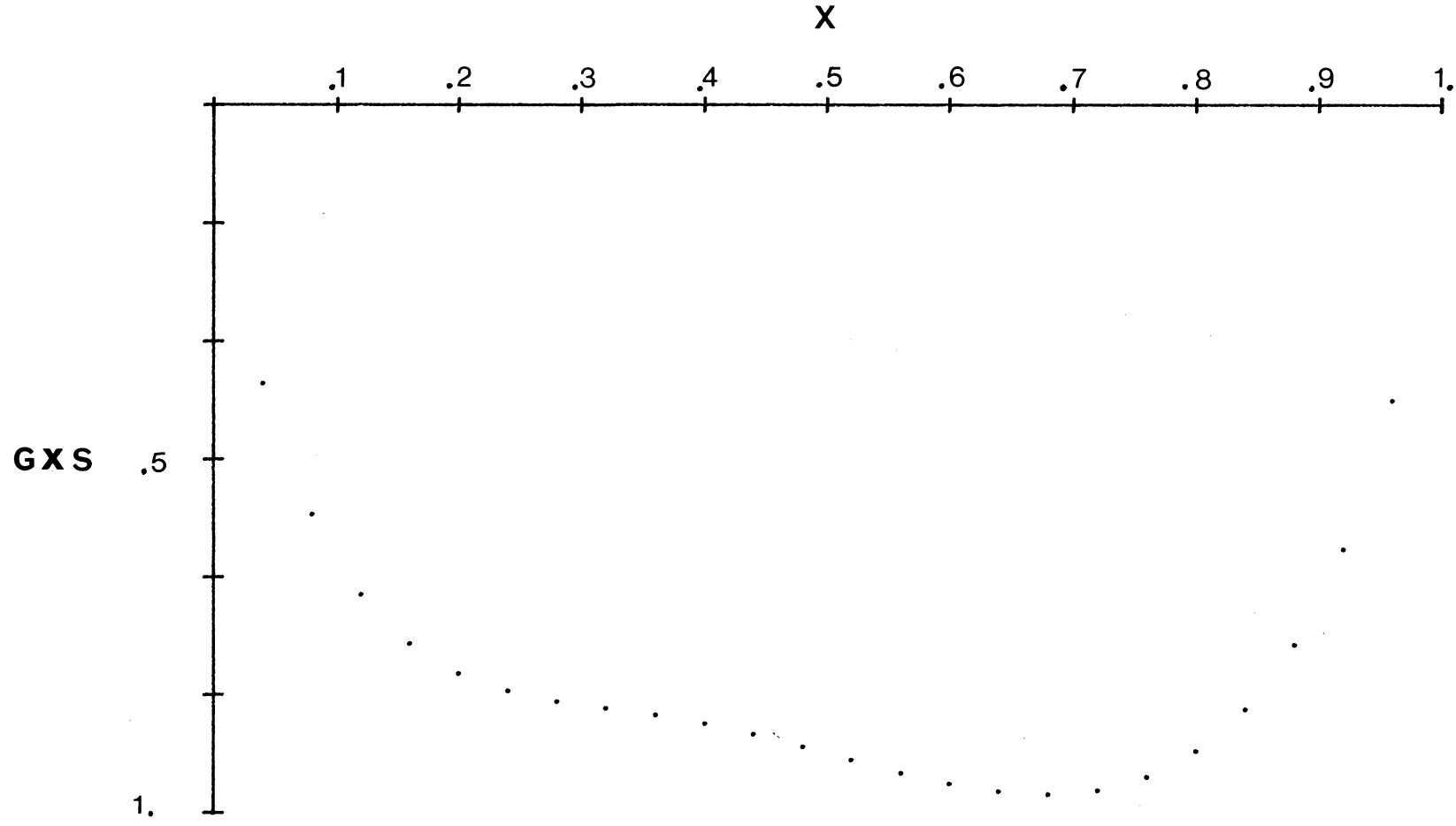


Figure 9

The composition plot of the Gibbs free energy for  $T^* = .48$ ,  
 $P^* = .002074$ ,  $W = .99$ ,  $GMIN = -.43$ . GXS is given in units of  
GMIN.

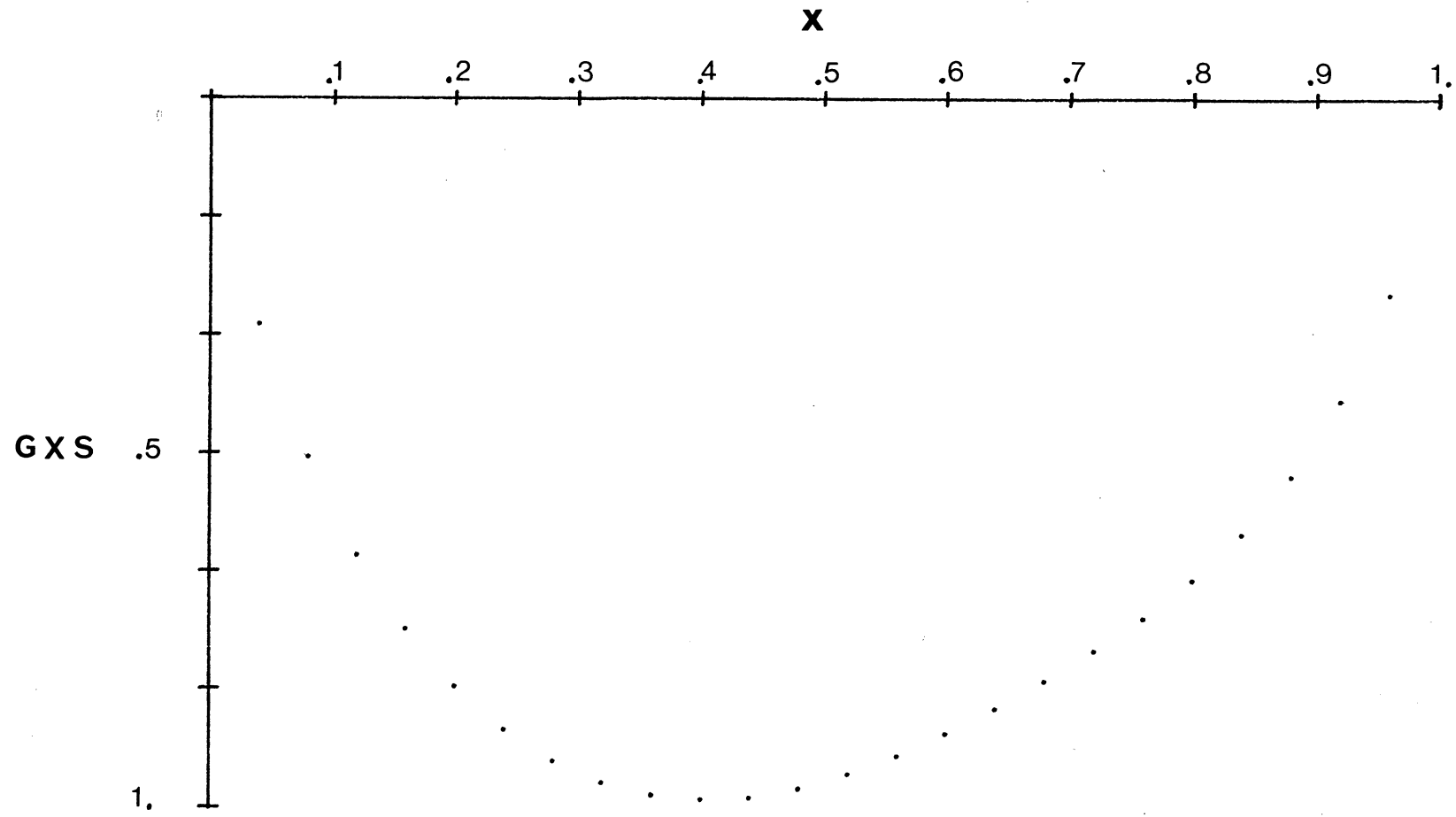


Figure 10

The composition plot of the Gibbs free energy for  $T^* = .18$ ,  
 $P^* = .001383$ ,  $W = 1.0$ ,  $GMIN = -.22$ .  $GXS$  is given in units of  
 $GMIN$ .

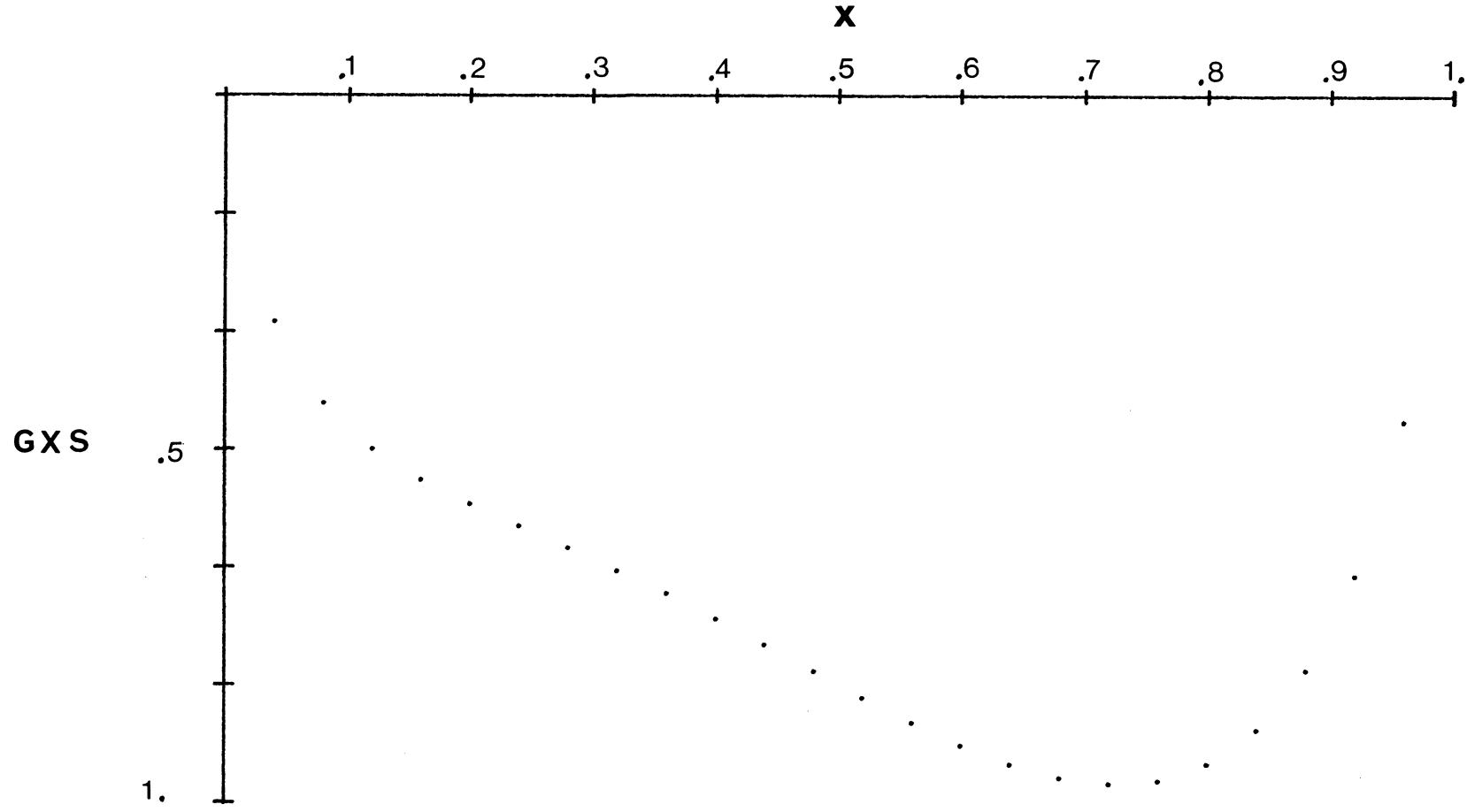


Figure 11

The composition plot of the Gibbs free energy for  $T^* = .28$ ,  
 $P^* = .001383$ ,  $W = 1.0$ ,  $GMIN = -.24$ . GXS is given in units of  
GMIN.

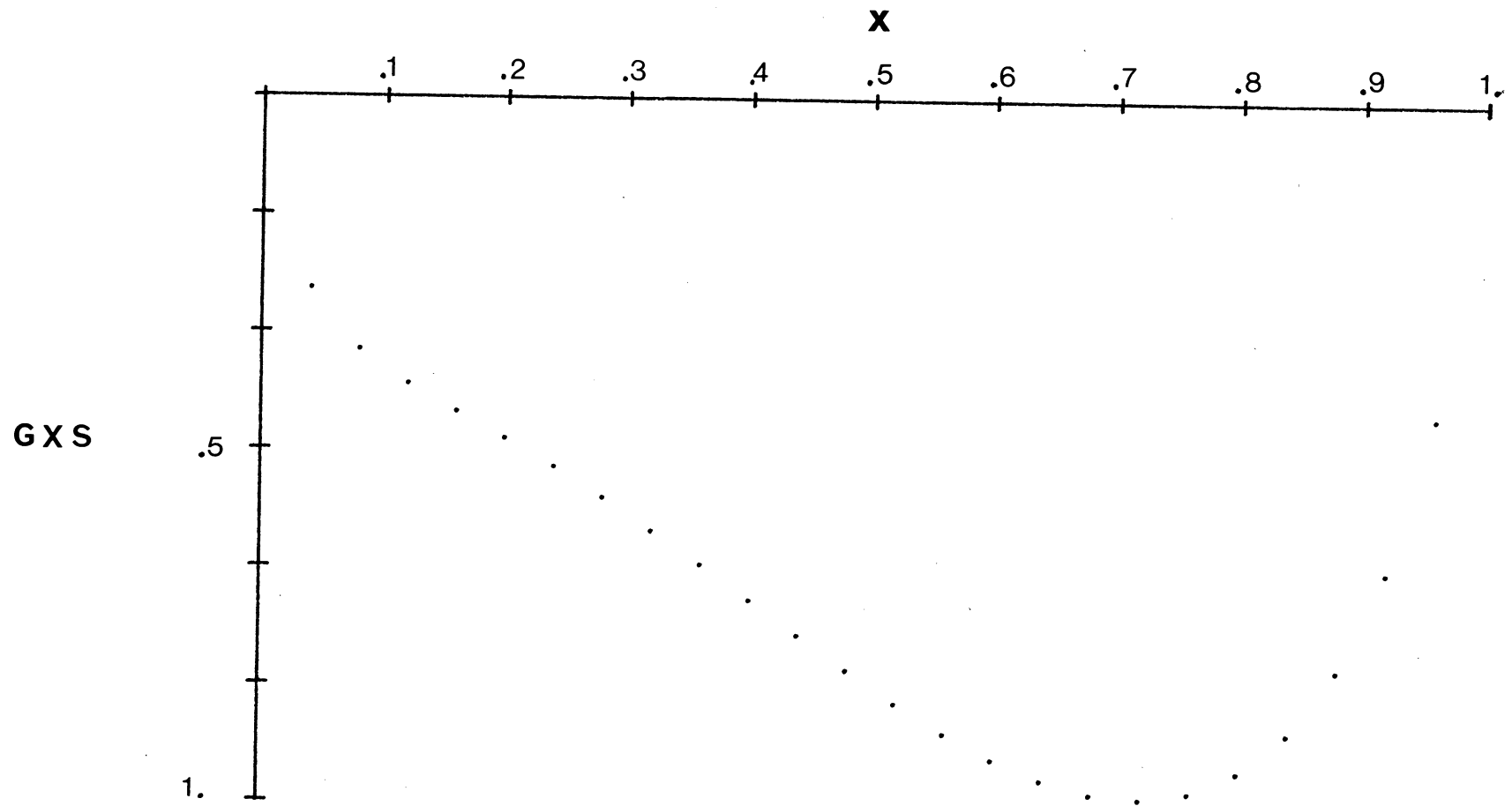


Figure 12

The composition plot of the Gibbs free energy for  $T^* = .38$ ,  
 $P^* = .001383$ ,  $W = 1.0$ ,  $GMIN = -.22$ . GXS is given in units of  
GMIN.

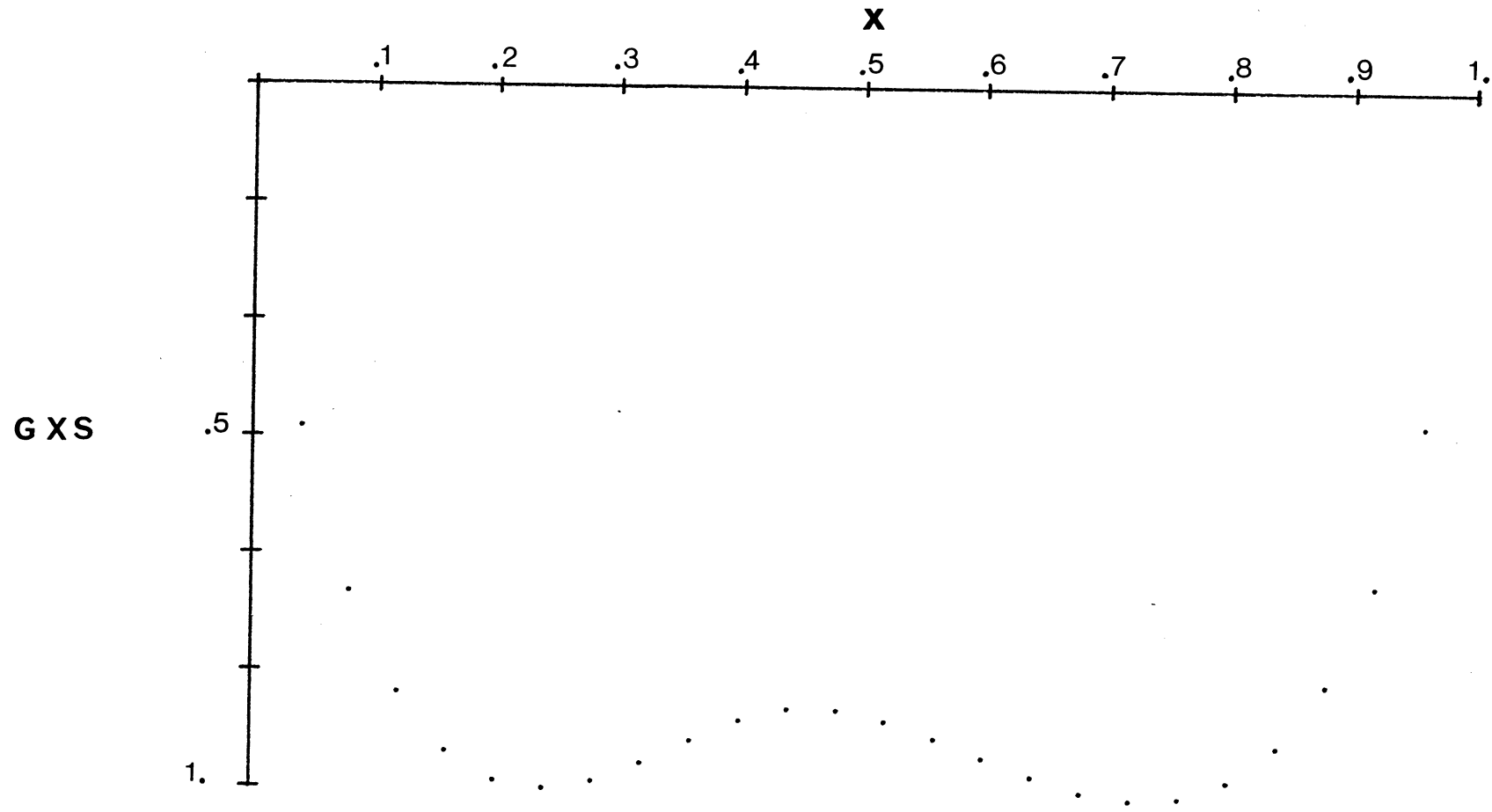


Figure 13

The composition plot of the Gibbs free energy for  $T^* = .48$ ,  
 $P^* = .001383$ ,  $W = 1.0$ ,  $GMIN = -.50$ . GXS is given in units of  
GMIN.

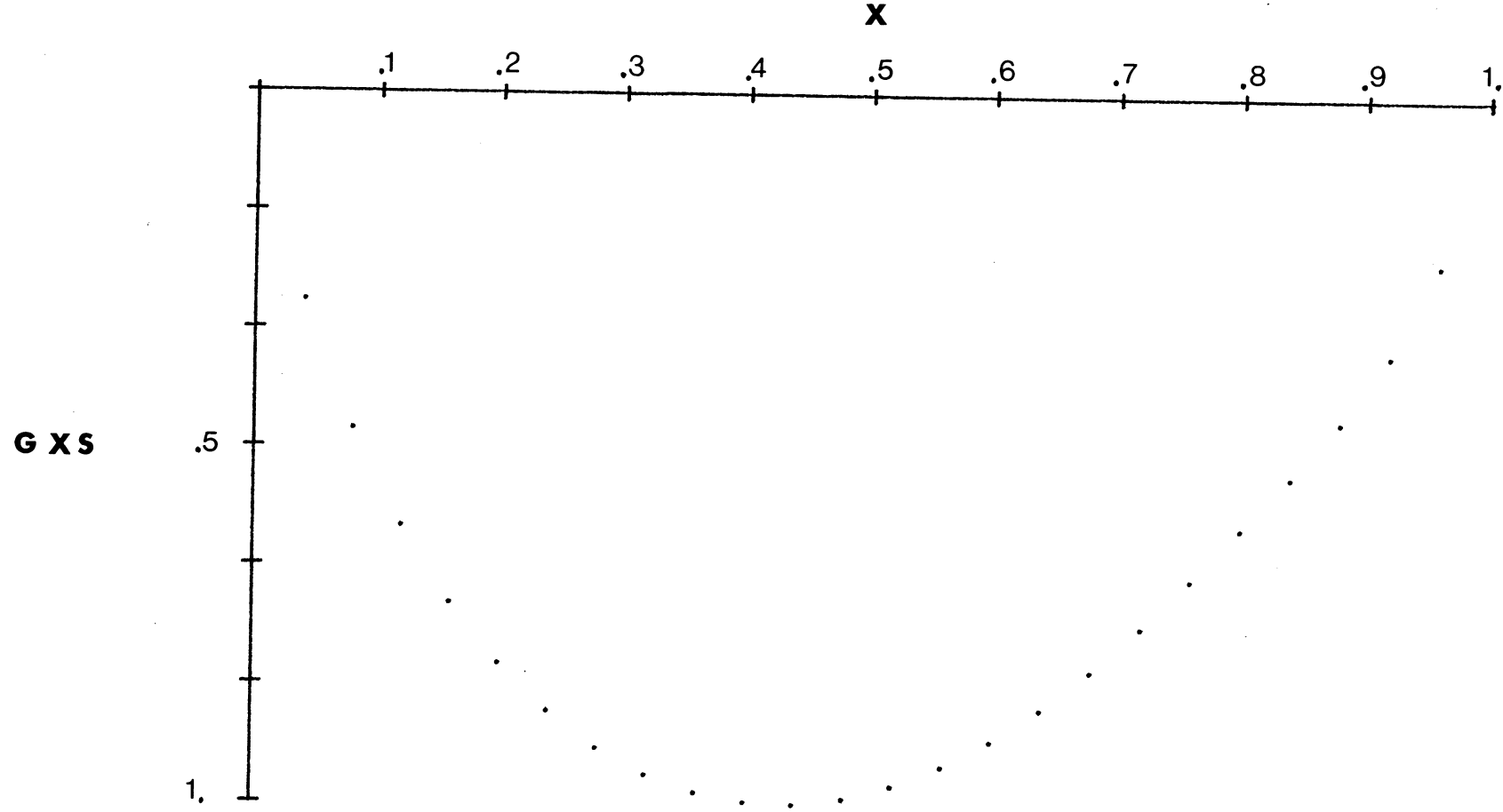


Figure 14

The composition plot of the Gibbs free energy for  $T^* = .18$ ,  
 $P^* = .002074$ ,  $W = 1.0$ ,  $GMIN = -.23$ . GXS is given in units of  
GMIN.

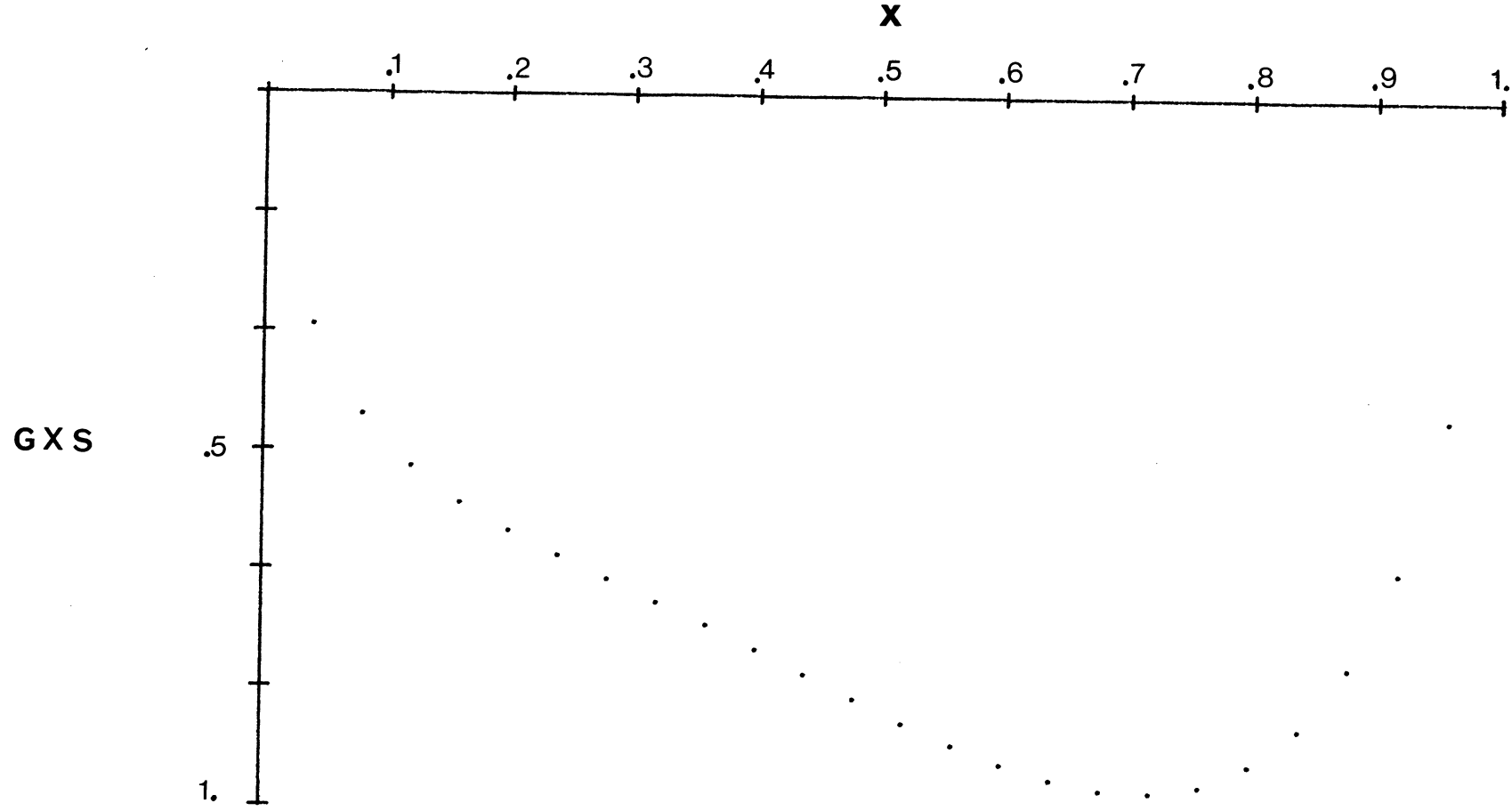


Figure 15

The composition plot of the Gibbs free energy for  $T^* = .28$ ,  
 $P^* = .002074$ ,  $W = 1.0$ ,  $GMIN = -.28$ . GXS is given in units of  
GMIN.

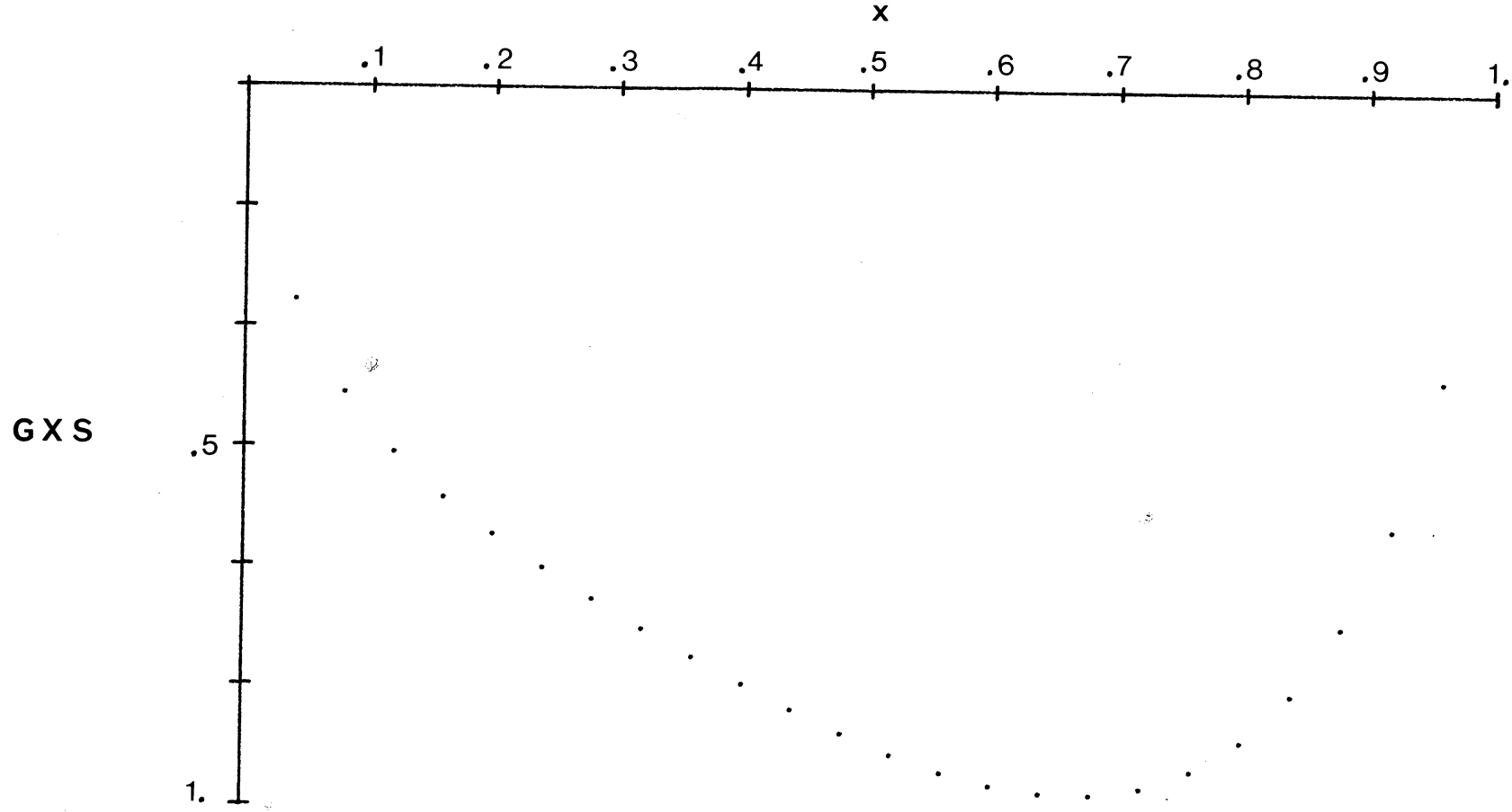


Figure 16

The composition plot of the Gibbs free energy for  $T^* = .38$ ,  
 $P^* = .002074$ ,  $W = 1.0$ ,  $GMIN = -.29$ . GXS is given in units of  
GMIN.

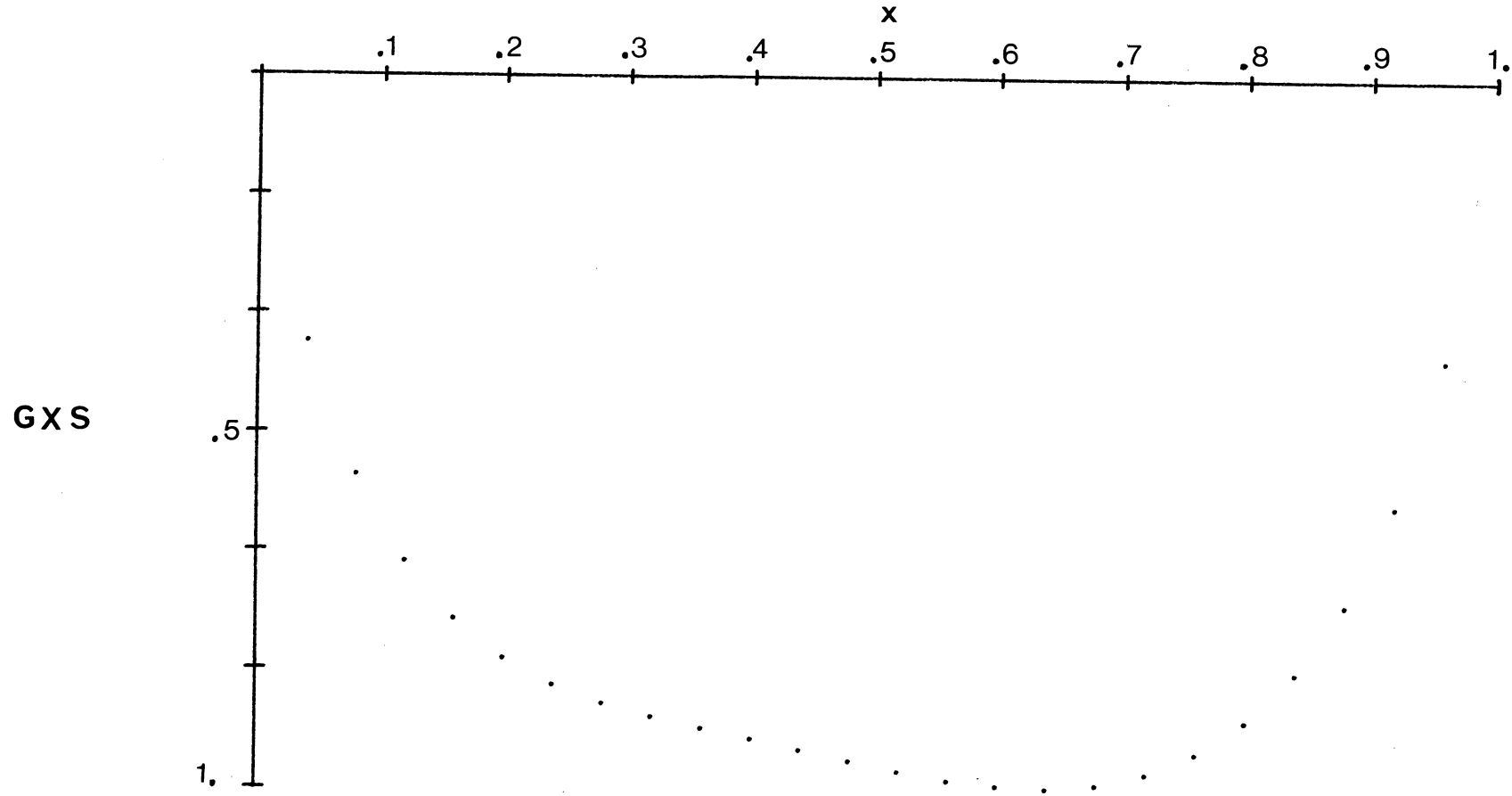


Figure 17

The composition plot of the Gibbs free energy for  $T^* = .46$ ,  
 $P^* = .002074$ ,  $W = 1.0$ ,  $GMIN = -.42$ . GXS is given in units of  
GMIN.

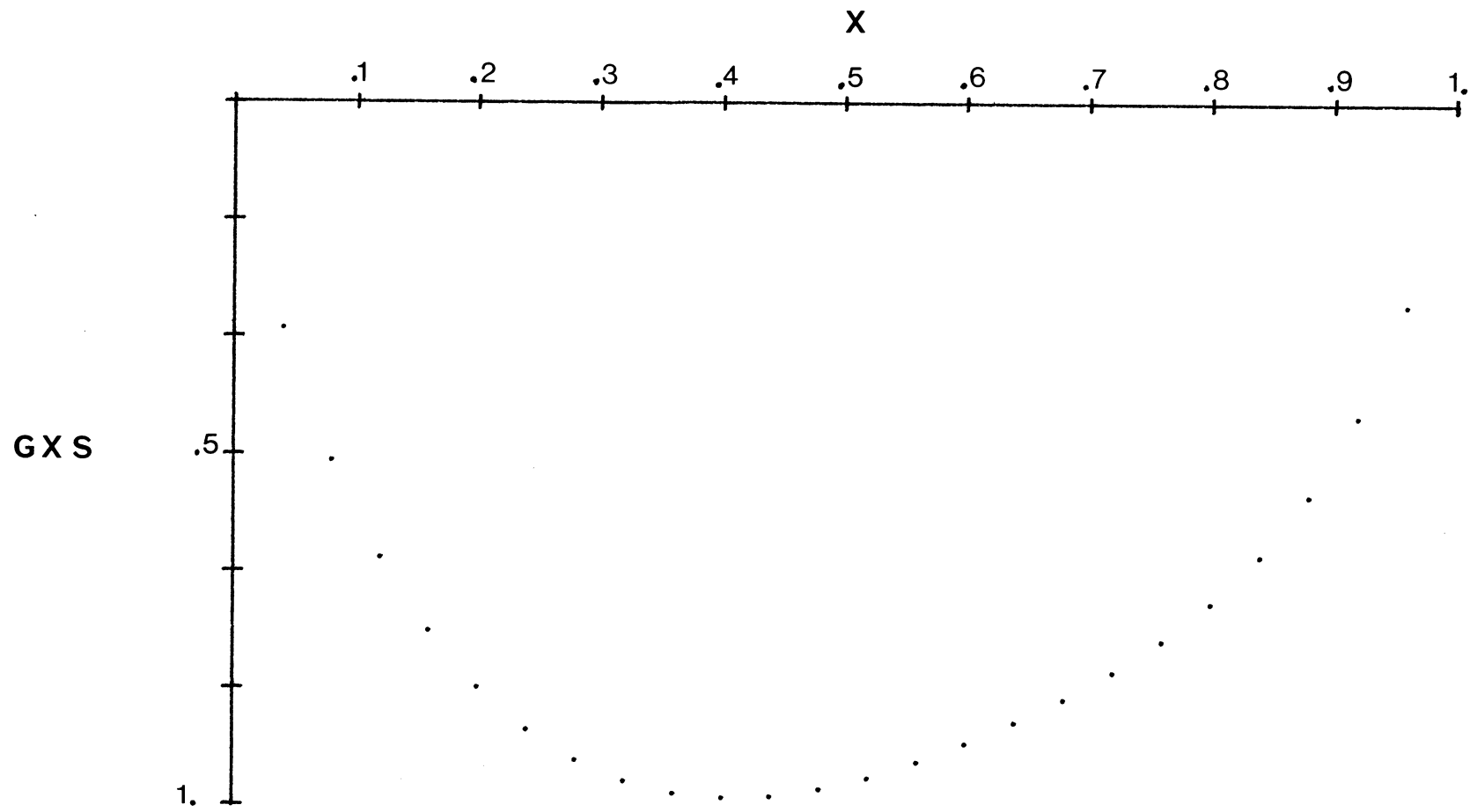


Figure 18

The composition plot of the Gibbs free energy for  $T^* = .18$ ,  
 $P^* = .001383$ ,  $W = 1.01$ ,  $GMIN = -.27$ . GXS is given in units of  
GMIN.

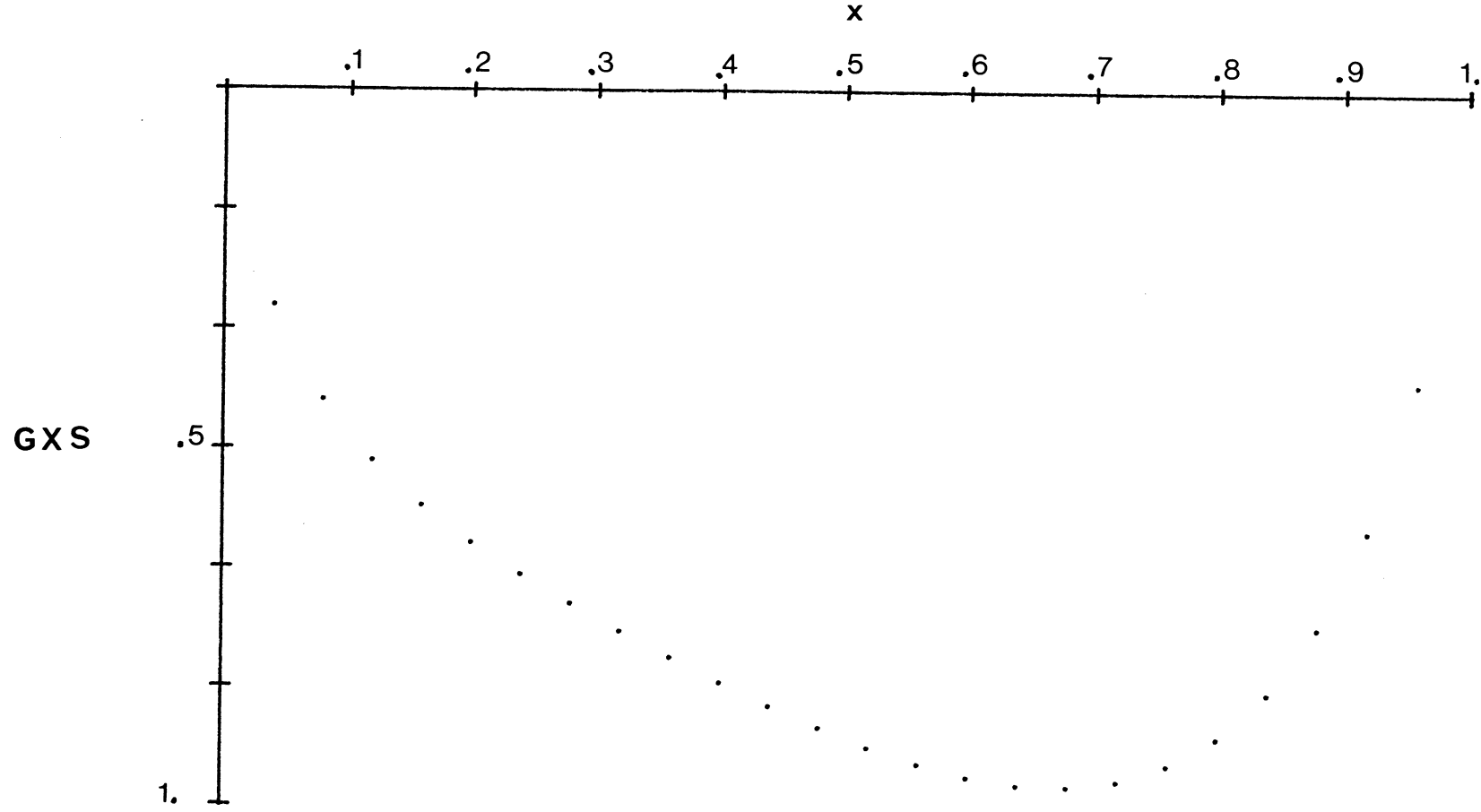


Figure 19

The composition plot of the Gibbs free energy for  $T^* = .28$ ,  
 $P^* = .001383$ ,  $W = 1.01$ ,  $GMIN = -.28$ . GXS is given in units of  
GMIN.

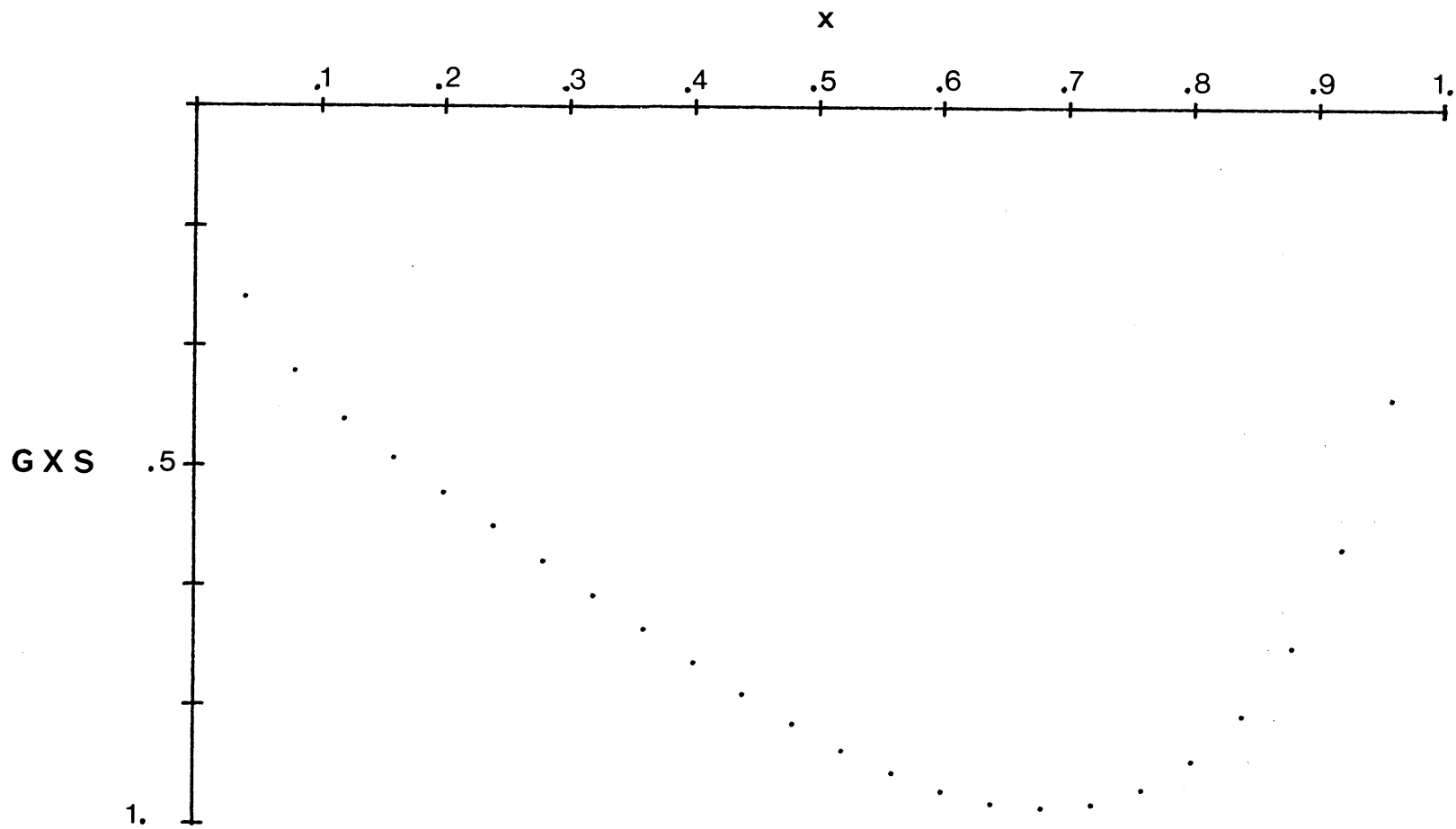


Figure 20

The composition plot of the Gibbs free energy for  $T^* = .38$ ,  
 $P^* = .001383$ ,  $W = 1.01$ ,  $GMIN = -.26$ . GXS is given in units of  
GMIN.

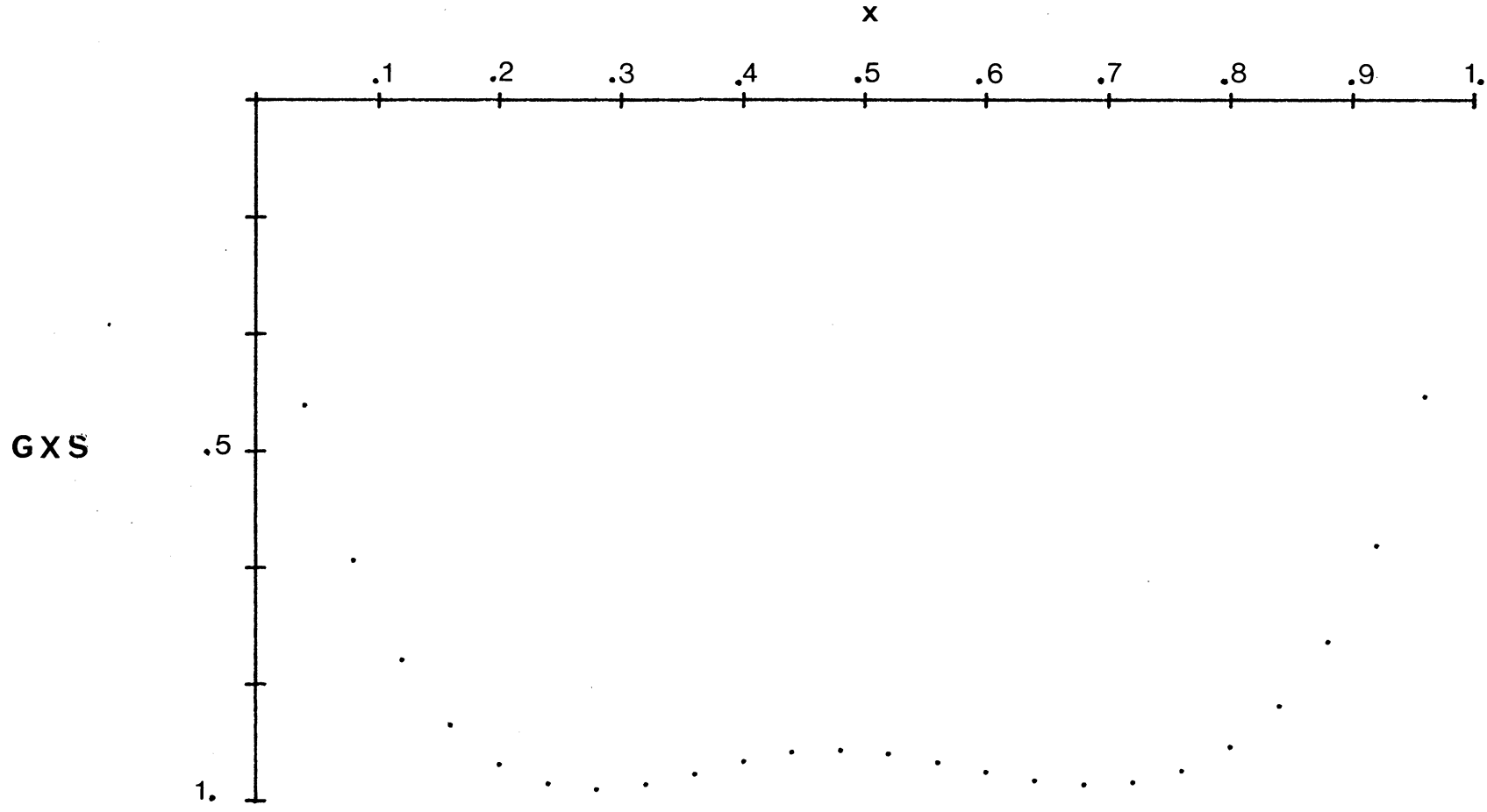


Figure 21

The composition plot of the Gibbs free energy for  $T^* = .48$ ,  
 $P^* = .001383$ ,  $W = 1.01$ ,  $GMIN = -.54$ . GXS is given in units of  
GMIN.

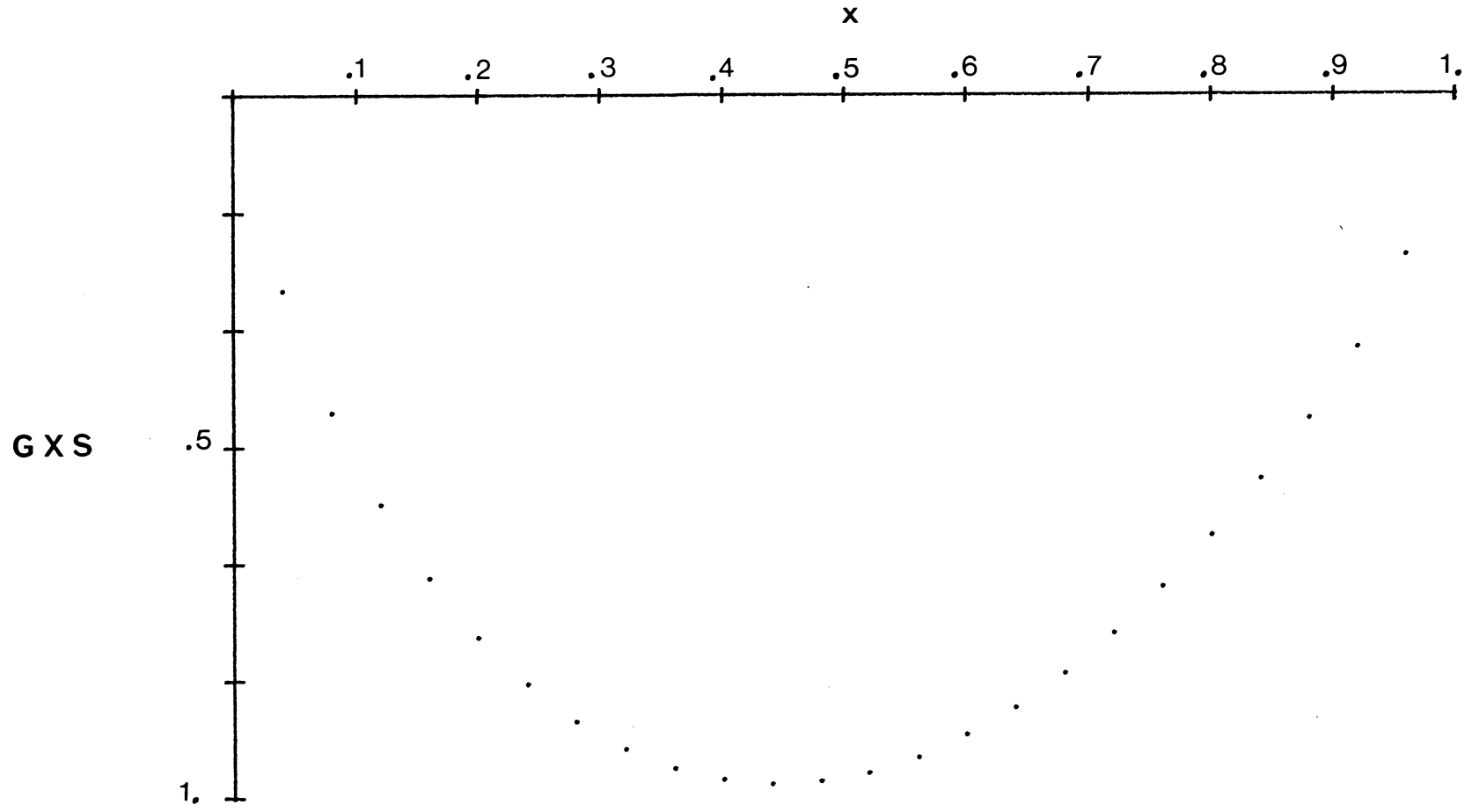


Figure 22

The composition plot of the Gibbs free energy for  $T^* = .18$ ,  
 $P^* = .002074$ ,  $W = 1.01$ ,  $GMIN = -.28$ . GXS is given in units of  
GMIN.

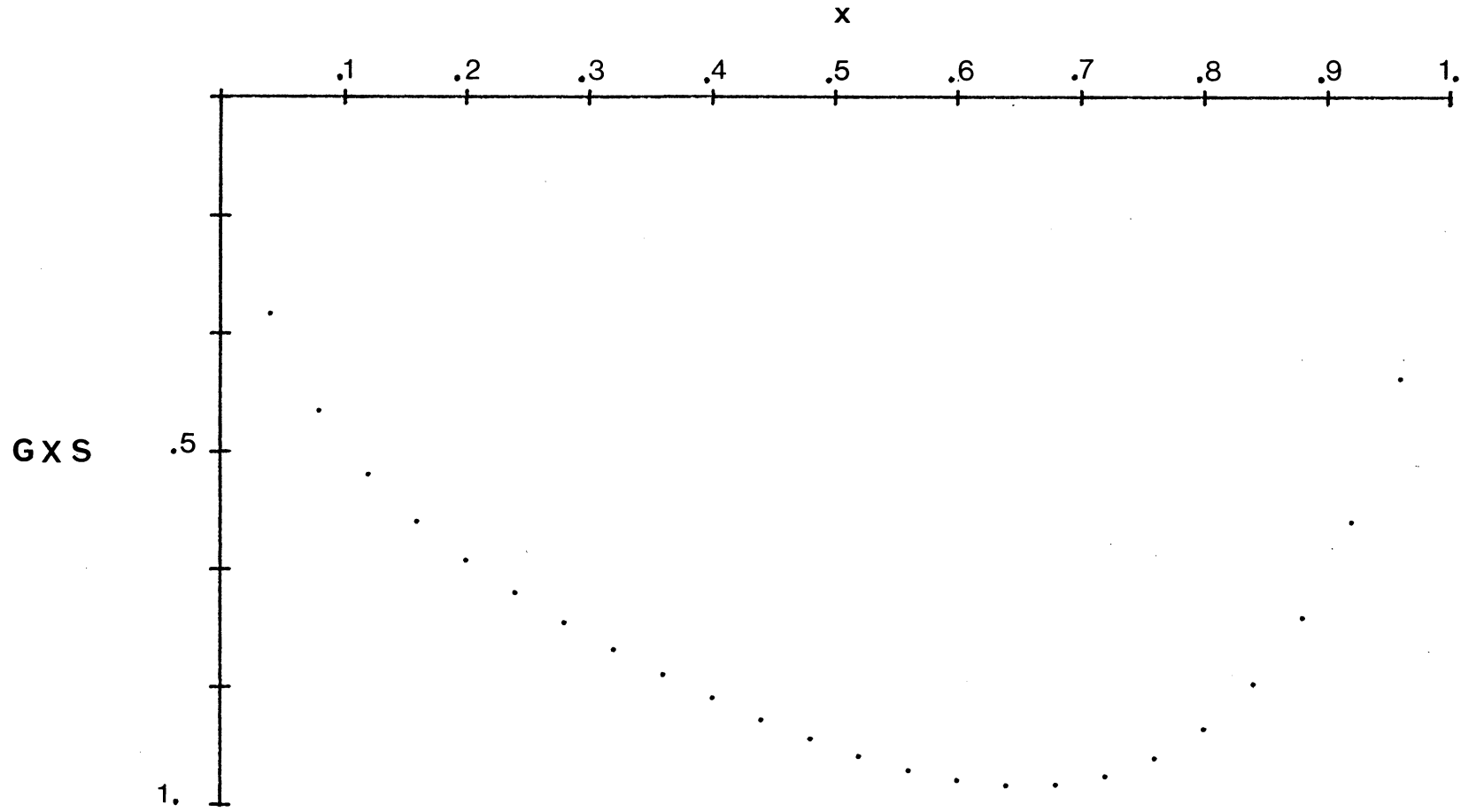


Figure 23

The composition plot of the Gibbs free energy for  $T^* = .28$ ,  
 $P^* = .002074$ ,  $W = 1.01$ ,  $GMIN = -.32$ . GXS is given in units of  
GMIN.

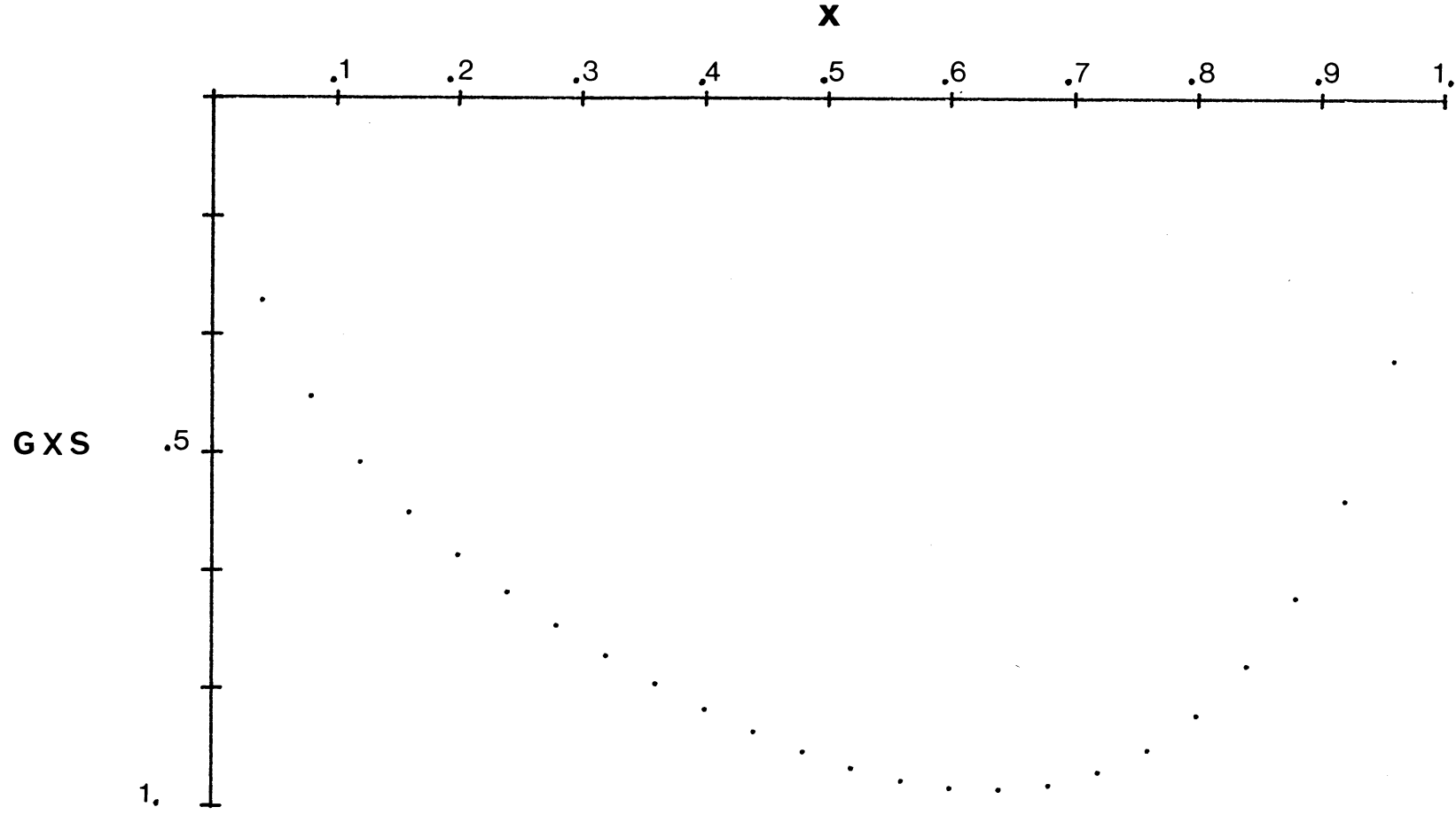


Figure 24

The composition plot of the Gibbs free energy for  $T^* = .38$ ,  
 $P^* = .002074$ ,  $W = 1.01$ ,  $GMIN = -.33$ . GXS is given in units of  
GMIN.

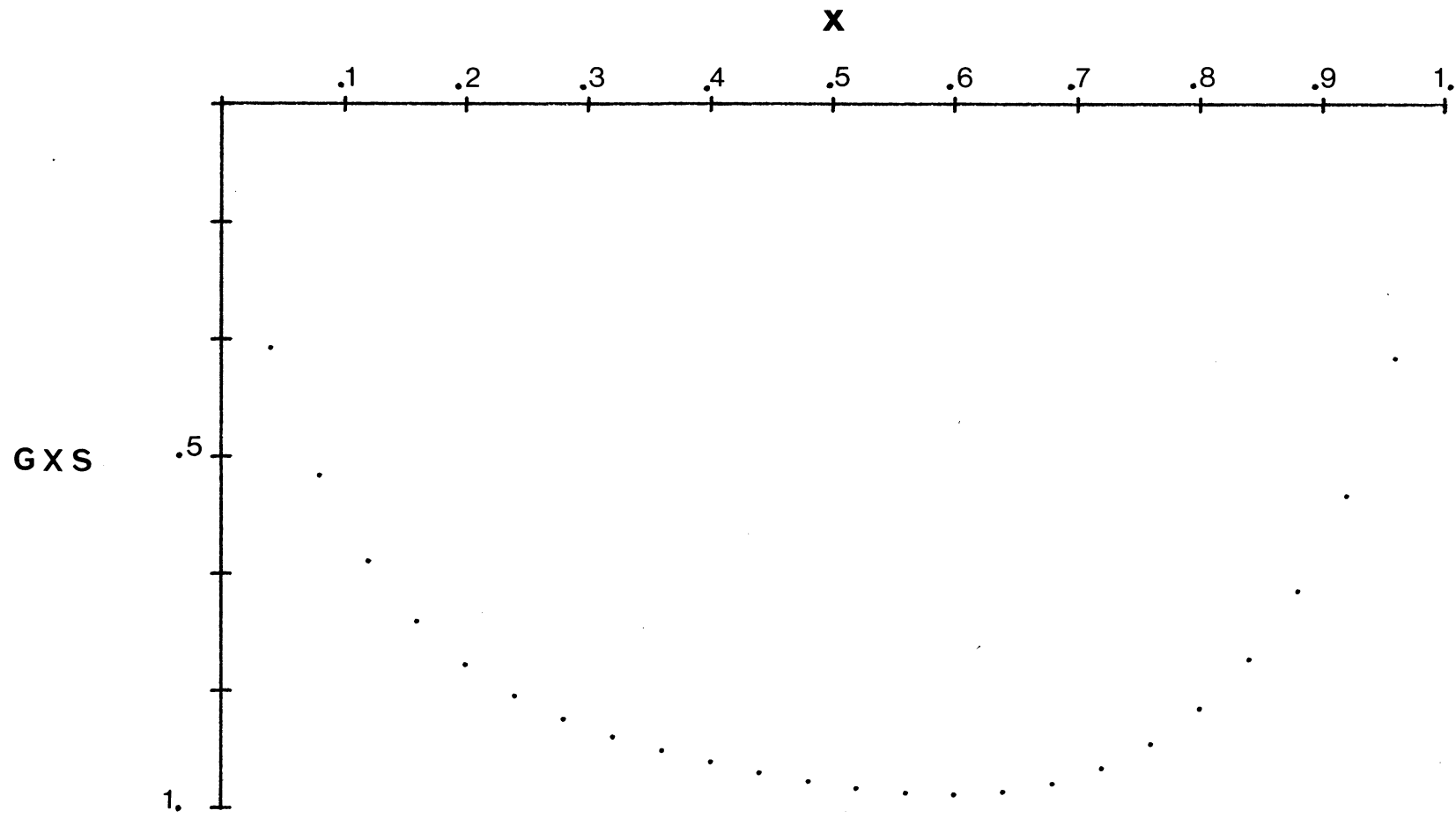


Figure 25

The composition plot of the Gibbs free energy for  $T^* = .48$ ,  
 $P^* = .002074$ ,  $W = 1.01$ ,  $GMIN = -.49$ . GXS is given in units of  
GMIN.

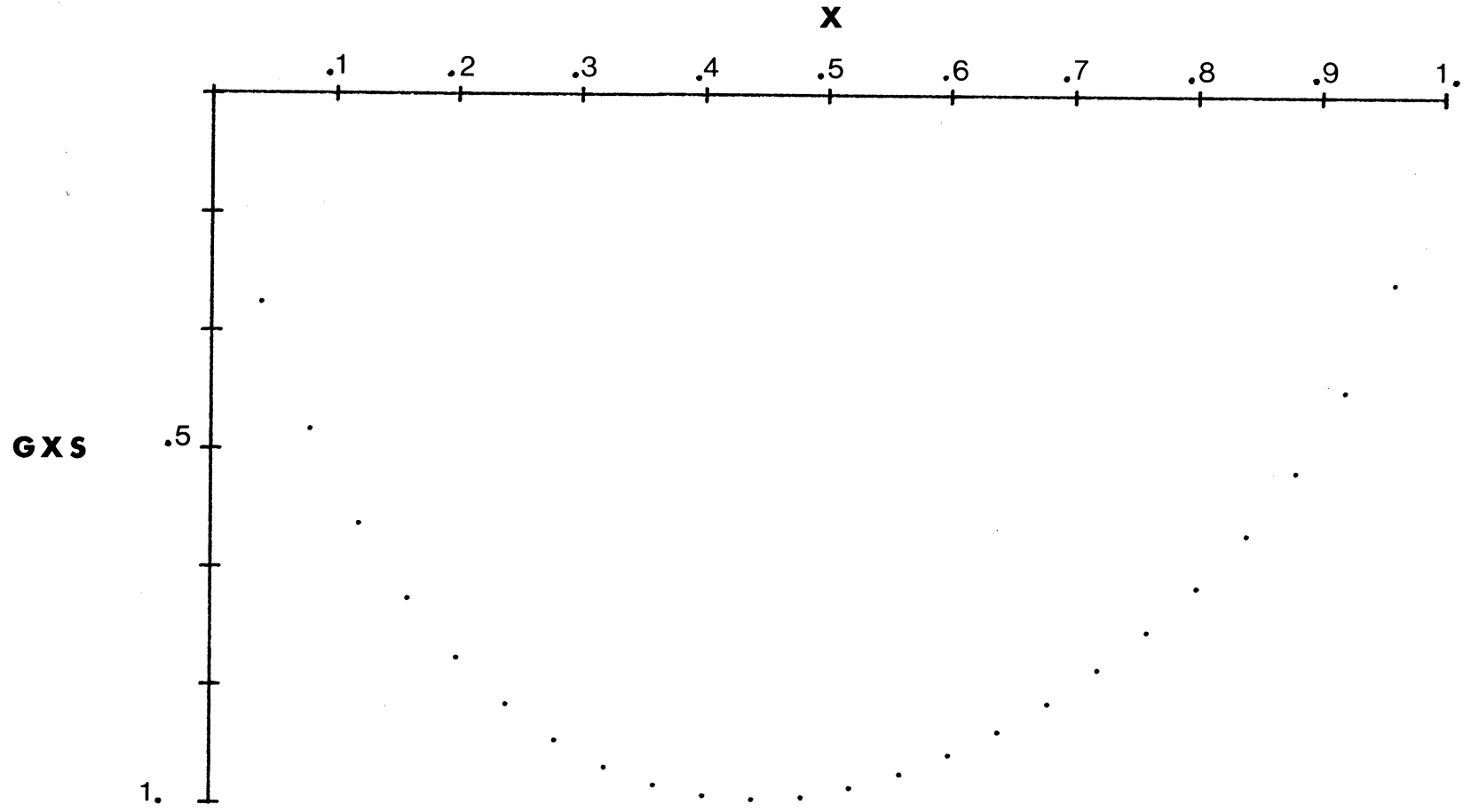


Figure 26

The temperature-composition plot of the mixture characterized by  
 $X_M = 1.5$ ,  $W = 1.01$  at  $P^* = .001383$  (.....) and  $P^* = .002074$   
(xxxxxxx).

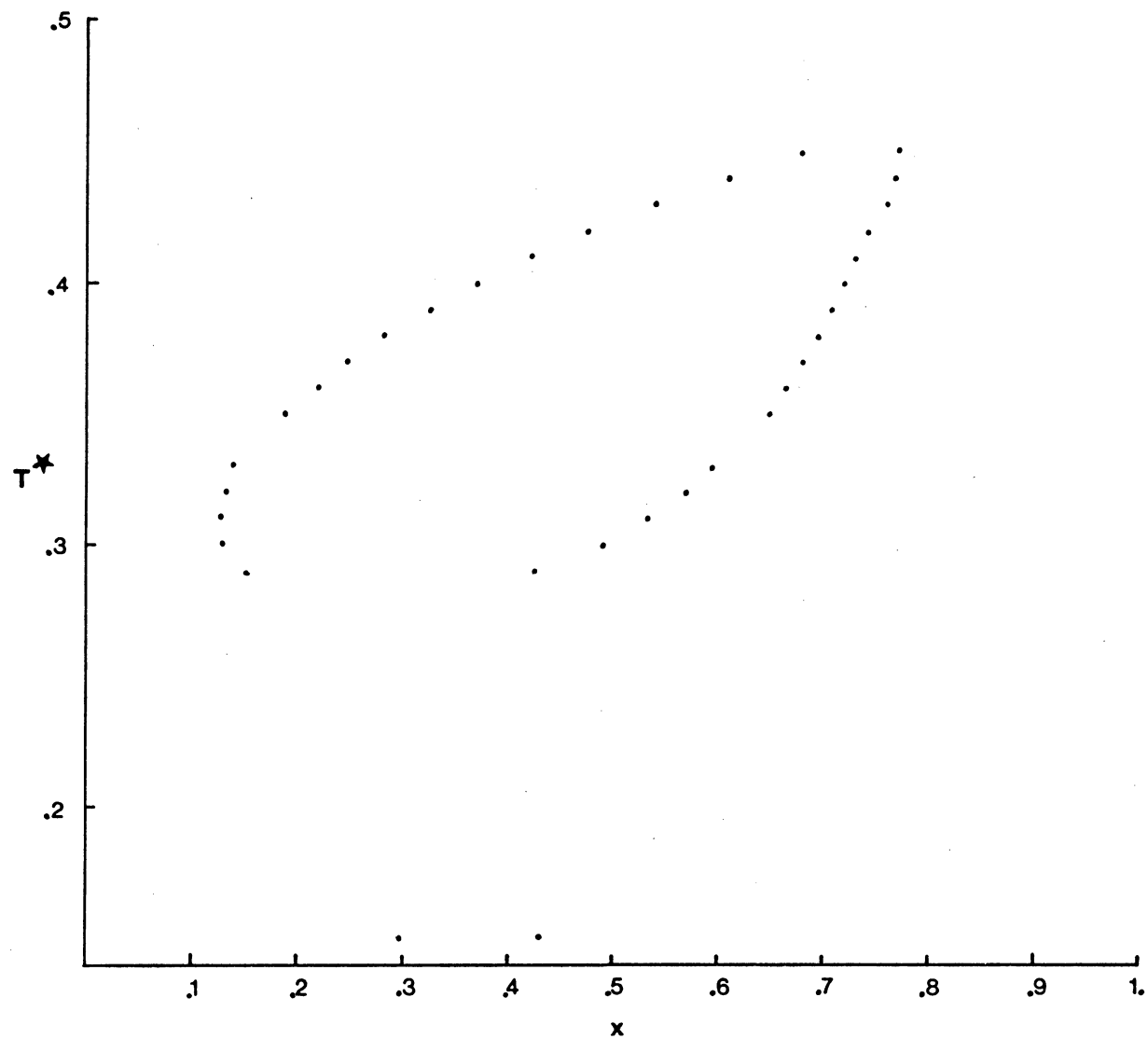


Figure 27

The temperature-composition plot of the mixture characterized by  
 $X_M = 1.5$ ,  $W = 1.00$  at  $P^* = .001383$  (.....) and  $P^* = .002074$   
(xxxxxxx).

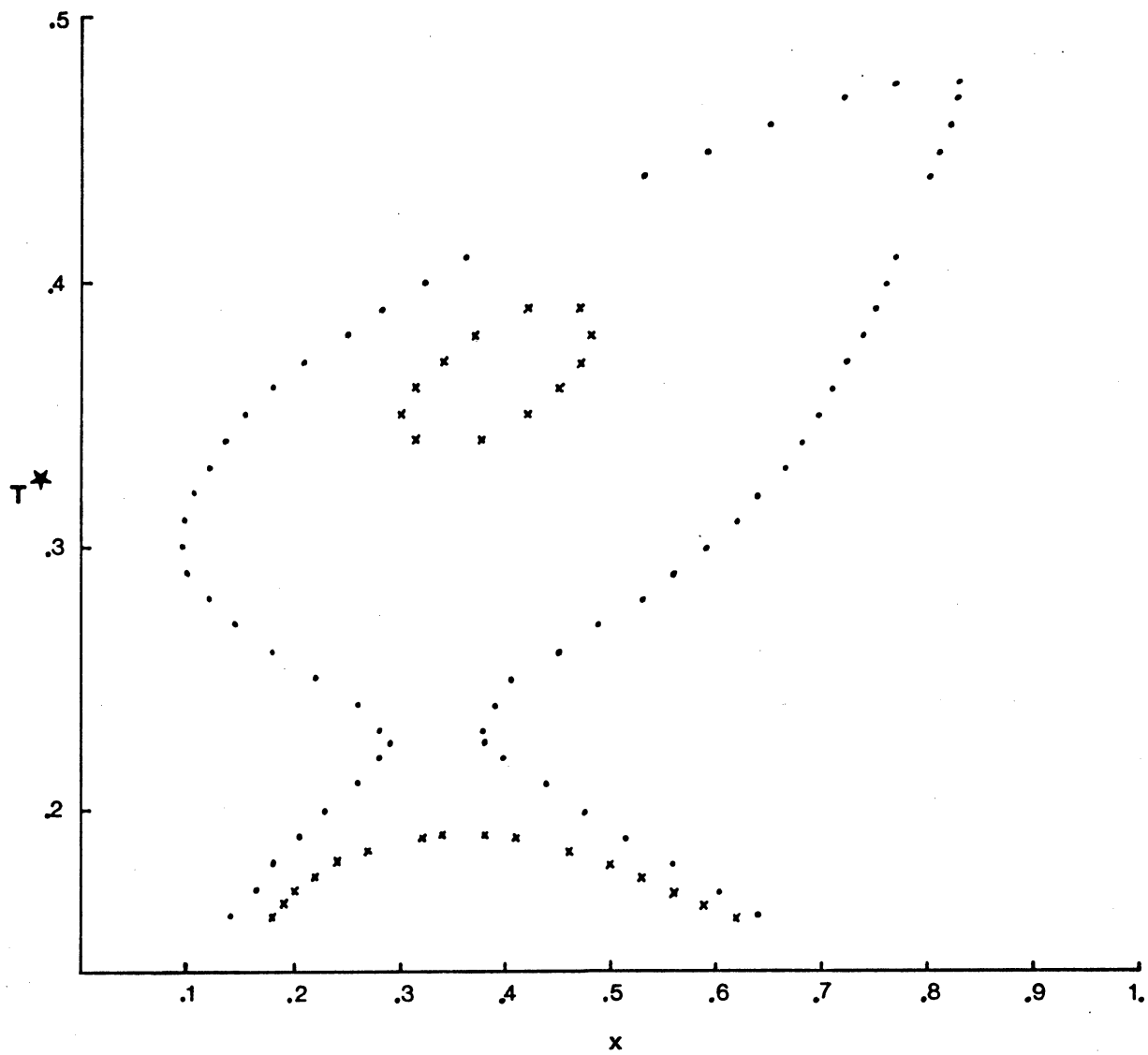
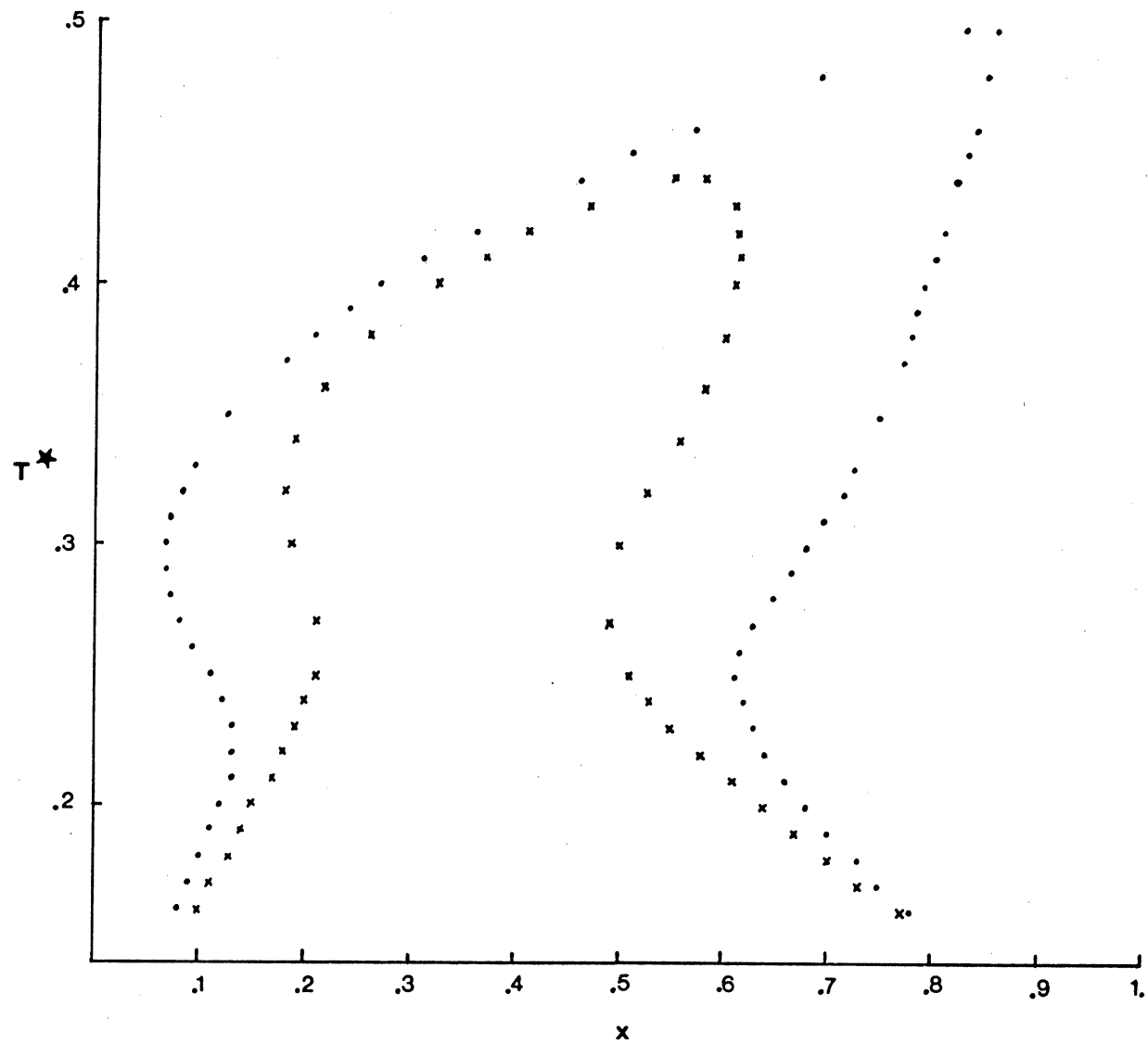


Figure 28

The temperature-composition plot of the mixture characterized by  
 $X_M = 1.5$ ,  $W = .99$  at  $P^* = .001383$  (.....) and  $P^* = .002074$  (xxxxxxx)



## Appendix 1

### Finite Volume Corrections to the Pair Correlation Function and the Helmholtz Free Energy

The calculation of the thermodynamic functions in Chapter 1 assumes that the finite volume (i.e., surface effects due to the long range nature of the potential and of the correlations) effects vanish in the thermodynamic limit. For convenience here, the thermodynamic limit will be taken to be the limiting behaviour of the property being considered in a finite volume  $V$  as  $V$  approaches infinity at constant density  $\rho$ . The requirement of constant  $\rho$  implies that  $N$  changes as  $\rho V$  as  $V \rightarrow \infty$ . The thermodynamic properties of the dipolar fluid in a spherical container of finite volume  $V$  are summarized in the Helmholtz free energy of the finite volume system. This will be calculated first and then the limiting large volume case considered afterwards.

The Helmholtz free energy of the dipolar fluid in excess of the "uncharged" hard sphere fluid is  $\Delta A$ , where a charging process involving the coupling parameter  $\lambda^{\frac{1}{2}} m$  gives the expression (Nienhuis and Deutch, 1974):

$$\Delta A = \frac{\rho^2}{32\pi^2} \int_0^1 d\lambda \int d\vec{r}_1 d\vec{s}_1 d\vec{r}_2 d\vec{s}_2 u(\vec{r}_{12}, \vec{s}_1, \vec{s}_2) h(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2; \lambda).$$

For a finite volume sample,

$$h(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2; \lambda) = h_\infty(\vec{r}_{12}, \vec{s}_1, \vec{s}_2; \lambda) + \Delta h(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2),$$

where  $h_\infty$  is the infinite volume result (equation (19), Chapter 2) and  $\Delta h$  is the finite volume correction of Wertheim which is

$$\Delta h = \frac{3y\beta m^2}{q(2\xi)q(-\xi)} (\vec{s}_1 \cdot \vec{\nabla}_1)(\vec{s}_2 \cdot \vec{\nabla}_2) \sum_{l=1}^{\infty} \frac{(l+1)}{(2l+1)} n_l Q_l(\vec{r}_1, \vec{r}_2),$$

where

$$n_l = -(2l+1)/[lq(2\xi) + (l+1)q(-\xi)],$$

$$Q_l = r_1^l r_2^l P_l(\cos \theta_{12})/A^{2l+1},$$

and  $y, q(2\xi), q(-\xi)$  are independent of volume. The result is specific for a spherical container of finite diameter  $A$ . From Chapter 2, equation (6) can be substituted for  $h_{\infty}$ , evaluation of the angular integration  $\int d\vec{\Omega}_1 d\vec{\Omega}_2 D(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) D(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) = 32\pi^2/3$  gives

$$\begin{aligned} \beta \Delta A &= -\frac{4\pi\beta m^2 \rho^2 V}{3} \int_0^1 d\lambda \int_R^A dr_{12} r_{12}^{-1} h_0(r_{12}; \lambda) \\ &+ \frac{\beta \rho^2 m^2}{32\pi^2} \int_0^1 d\lambda \int d\vec{r}_1 d\vec{\Omega}_1 d\vec{r}_2 d\vec{\Omega}_2 \Delta h r_{12}^{-3}. \end{aligned}$$

The restriction on the spatial configurations in the second term is

$r_1 < A$ ,  $r_2 < A$  and  $r_{12} > R$ . If the limit  $V \rightarrow \infty$  were now taken, the Helmholtz free energy of the infinite system would go to infinity as  $V$ . However the free energy per particle  $N$  is bounded and is found to be

$$\begin{aligned} \lim_{\substack{V \rightarrow \infty \\ \rho \text{ fixed} \\ N = \rho V}} \frac{\beta \Delta A}{N} &= -\frac{4\pi\beta m^2 \rho}{3} \int_0^1 d\lambda \kappa(\lambda) \\ &+ \lim_{\substack{V \rightarrow \infty \\ \rho \text{ fixed} \\ N = \rho V}} \frac{\beta m^2 \rho^2}{32\pi^2 N} \int_0^1 d\lambda \int d\vec{r}_1 d\vec{\Omega}_1 d\vec{r}_2 d\vec{\Omega}_2 \Delta h r_{12}^{-3}, \end{aligned}$$

where  $\kappa(\lambda) = \lim_{V \rightarrow \infty} \int_R^{V^{1/3}} dr r^{-1} h^p(r; \lambda)$  . The first term is the infinite volume result of Nienhuis and Deutch. The finite volume correction to the Helmholtz free energy per particle vanishes in the limit  $V \rightarrow \infty$  . This is seen in the following argument.

$\Delta h$  is of the order  $V^{-1} \sim A^{-3}$  from  $\nabla_1 \nabla_2 Q_L = O((r_1^{\ell-1} r_2^{\ell-1})/A^{2\ell+1}) = O(A^{-3})$  for  $r_1, r_2 = O(A)$  . Then the integrations over  $\vec{r}_1$  and  $\vec{r}_2$  can be changed to  $\vec{r}_{12}$  and  $\vec{r}_2$  since we are only interested in an order of magnitude calculation involving the translationally invariant  $\Delta h$  . Using

$$\int d\vec{r}_1 d\vec{r}_2 r_{12}^{-3} \Delta h \sim A^{-3} A^3 \int_R^A d r_{12} r_{12}^{-1} \sim \ln(V^{1/3}/R),$$

one is lead to seeing that the finite volume correction goes as

$N^{-1} \ln(V^{1/3}/R) = (V\rho)^{-1} \ln(V^{1/3}/\rho)$  as  $V \rightarrow \infty$  . From L'Hospital's rule  $V^{-1} \ln V \rightarrow 0$  as  $V \rightarrow \infty$  . Thus the thermodynamic limit of the Helmholtz free energy per particle  $\beta \Delta A/N$  is given by consideration of the infinite volume distribution function result in the calculation. No surface effects are important in the mechanical thermodynamic properties of the system as can be shown by repeating the foregoing analysis. Therefore the internal energy per particle, the Helmholtz free energy per particle, and the pressure are correctly described by consideration of the distribution function of the infinite system only. This is in distinct contrast to the calculation of the dielectric constant by Wertheim where the finite volume correction to the distribution function is of paramount importance. The generalization to the multicomponent case seems immediate.

## Appendix 2

### The Operational Methods of Wertheim

This Appendix gives a lengthy discussion on a possible motivation for the introduction of the operator formalism of Wertheim. The motivation is given by the consistency of the Hankel inversion of the equations for the Fourier components  $h^{mne}(k)$  and  $c^{mne}(k)$ . The Fourier transform of the indirect correlation function  $h(\Omega_1, \Omega_2, r)$  can be written (Blum and Torruella, 1972; Adelman and Deutch, 1973) as  $\tilde{h}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{k})$  where

$$\tilde{h}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{k}) = \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} h(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}). \quad (2.1)$$

Using the invariant expansion of  $h(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r})$  in terms of the  $\phi^{mne}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r)$ , the integration over orientations of the  $\vec{r}$  direction,  $\vec{\Omega}_r$ , is carried out using the Rayleigh expansion of  $e^{i\vec{k} \cdot \vec{r}}$  in terms of the generalized spherical harmonics,  $D_{mn}^l(\vec{\Omega}_r)$  (Abramowitz and Stegun, 1968). Substitution of

$$e^{i\vec{k} \cdot \vec{r}} = \sum_{l=0}^{\infty} \sum_{|m| \leq l} (2l+1) i^l j_l(kr) D_{m0}^l(\vec{\Omega}_k) D_{m0}^{l*}(\vec{\Omega}_r)$$

where  $j_l(kr)$  is spherical Bessel function of order  $l$  and  $k = |\vec{k}|$  into equation (2.1) enables the orthogonality of the  $D_{mn}^l(\vec{\Omega}_r)$ 's to be used in the integration over  $\vec{\Omega}_r$ . This gives

$$\tilde{h}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{k}) = \sum_{m,n,l} h^{mne}(k) \phi^{mne}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_k) \quad (2.2)$$

where  $h^{mne}(k)$  is the one dimensional Hankel transform of  $h^{mne}(r)$  of order  $l$ ,

$$h^{mne}(k) = 4\pi i^l \int_0^{\infty} dr r^2 j_l(kr) h^{mne}(r). \quad (2.3)$$

Use of (2.2) in the Ornstein Zernike equation, followed by projecting out the  $\phi^{mne}$  dependence gives equation (8) of Chapter 2. In the case of the Mean Spherical Approximation for a fluid of dipolar hard spheres, it can be seen from equations (13a) and (13b) of Chapter 2 that there are products of Hankel transforms of mixed order,  $l = 0$  and  $l = 2$ . Thus, Hankel inversion of these equations is not straightforward. A consistent inversion scheme is accomplished by inverting both equations with respect to the zeroth order Hankel transform. The inversion of  $h^D(k) [h^{112}(k)]$  with respect to  $j_0(kr)$  then defines a new function  $\hat{h}^D(r)$  as

$$\hat{h}^D(r) = (2\pi^2)^{-1} \int_0^\infty dk k^2 j_0(kr) h^D(k), \quad (2.4)$$

where

$$h^D(k) = -4\pi \int_0^\infty dr r^2 j_2(kr) h^D(r). \quad (2.5)$$

The Hankel-Bessel transform of  $\hat{h}^D(r)$  is  $\hat{h}^D(k)$  and, by definition, is given by

$$\hat{h}^D(k) = 4\pi \int_0^\infty dr r^2 j_0(kr) \hat{h}^D(r). \quad (2.6)$$

The substitution of equation (2.4) for  $\hat{h}^D(r)$  in equation (2.6) and use of the Hankel-Bessel inversion theorem gives the identity of  $\hat{h}^D(k)$  and  $h^D(k)$ :

$$\hat{h}^D(k) = h^D(k).$$

Multiplying this equality by  $D(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)$ , it can be seen that  $\hat{h}^0(K) D_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)$  and  $h^0(K) D_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)$  give identical contributions to  $h(\vec{\Omega}_1, \vec{\Omega}_2, \vec{K})$ . However, the Fourier inversion of these equivalent contributions give quite different representations of the corresponding contributions to  $h(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r})$ . The equivalence of these contributions in r-space and the use of the Hankel-Bessel transform of order  $l = 0$  (equation (2.6)) for the  $\hat{h}^0(K)$  term provides a possible motivation for Wertheim's operational techniques.

Fourier inversion of  $h^0(K) D_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)$  gives  $h^0(r) D(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r)$  trivially. However Fourier inversion of  $\hat{h}^0(K) D_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)$ , which is equivalent to inversion of equation (2.13) multiplied by  $D_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)$ , gives Wertheim's operational approach. The substitution of  $D_K = \vec{\Omega}_1 \cdot (3 \hat{K} \hat{K} - \mathcal{U}) \cdot \vec{\Omega}_2$  into the integral giving the Fourier inversion of  $\hat{h}^0(K) D_K$  is given below:

$$\begin{aligned} I_D &\equiv \int dK e^{-i\vec{K} \cdot \vec{r}} \hat{h}^0(K) D_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) \\ &= \int_0^\infty dK K^2 \hat{h}^0(K) \vec{\Omega}_1(\vec{\Omega}_1) \cdot \left[ \int d\vec{\Omega}_K (3 \hat{K} \hat{K} - \mathcal{U}) e^{-i\vec{K} \cdot \vec{r}} \right] \cdot \vec{\Omega}_2(\vec{\Omega}_2). \end{aligned}$$

The right hand side of  $I_D$  can be rearranged in terms of  $\vec{K}$  rather than  $\hat{K}$  giving

$$I_D = \vec{\Omega}_1(\vec{\Omega}_1) \cdot \left[ \int_0^\infty dK \hat{h}^0(K) \int d\vec{\Omega}_K (3 \vec{K} \vec{K} - K^2 \mathcal{U}) e^{-i\vec{K} \cdot \vec{r}} \right] \cdot \vec{\Omega}_2(\vec{\Omega}_2)$$

In order to introduce the  $\vec{\nabla}$  operator in Wertheim's analysis (Wertheim, 1971), the following identities are employed in the integrand of the integral over  $\vec{\kappa}$ :

$$\begin{aligned}\vec{\nabla} \vec{\nabla} e^{-i\vec{\kappa} \cdot \vec{r}} &= -\vec{\kappa} \vec{\kappa} e^{-i\vec{\kappa} \cdot \vec{r}} \\ \nabla^2 e^{-i\vec{\kappa} \cdot \vec{r}} &= -\kappa^2 e^{-i\vec{\kappa} \cdot \vec{r}}.\end{aligned}$$

These equalities follow directly from  $\vec{\nabla} e^{-i\vec{\kappa} \cdot \vec{r}} = -i\vec{\kappa} e^{-i\vec{\kappa} \cdot \vec{r}}$ .

The integral  $I_0$  can then be written as

$$\begin{aligned}I_0 &= -\vec{s}_1(\vec{\Omega}_1) \cdot \left[ \int_0^\infty d\kappa \hat{h}^D(\kappa) (3\vec{\nabla} \vec{\nabla} - \nabla^2) \int d\vec{\Omega}_\kappa e^{-i\vec{\kappa} \cdot \vec{r}} \right] \cdot \vec{s}_2(\vec{\Omega}_2) \\ &= -4\pi \vec{s}_1(\vec{\Omega}_1) \cdot (3\vec{\nabla} \vec{\nabla} - \nabla^2) \cdot \vec{s}_2(\vec{\Omega}_2) \int_0^\infty d\kappa \hat{h}^D(\kappa) j_0(\kappa r).\end{aligned}$$

The final integral over  $\kappa$  is not quite the Hankel inverse transform for  $\hat{h}^D(r)$ : a factor of  $\kappa^2$  is missing. Defining  $H^D(\kappa) = -\hat{h}^D(\kappa)/\kappa^2$  allows the Hankel inverse transform of  $H^D(\kappa)$  to be carried out,  $I_0$

$I_0$  can then be written in terms of  $H^D(r)$  and  $\vec{\nabla}$  as

$$\begin{aligned}I_0 &= -4\pi \vec{s}_1(\vec{\Omega}_1) \cdot (3\vec{\nabla} \vec{\nabla} - \nabla^2) \cdot \vec{s}_2(\vec{\Omega}_2) \int_0^\infty d\kappa \kappa^2 \frac{\hat{h}^D(\kappa)}{\kappa^2} j_0(\kappa r) \\ &= 4\pi \vec{s}_1(\vec{\Omega}_1) \cdot (3\vec{\nabla} \vec{\nabla} - \nabla^2) \cdot \vec{s}_2(\vec{\Omega}_2) \int_0^\infty d\kappa \kappa^2 H^D(\kappa) j_0(\kappa r) \\ &= \mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\nabla}) H^D(r)\end{aligned}$$

where

$$H^D(r) = 4\pi \int_0^\infty d\kappa \kappa^2 H^D(\kappa) j_0(\kappa r),$$

$$\mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\nabla}) = \vec{s}_1(\vec{\Omega}_1) \cdot (3\vec{\nabla} \vec{\nabla} - \nabla^2) \cdot \vec{s}_2(\vec{\Omega}_2),$$

and

$$k^2 H^D(k) = - \hat{h}^D(k) \quad (2.7)$$

The analogue of equation (2.7) in  $r$  space provides a relationship between  $H^D(r)$  and  $\hat{h}^D(r)$ . Equation (2.7) can be inverted with respect to the zeroth-order Hankel transform to give

$$\begin{aligned} \int_0^\infty dk k^2 j_0(kr) k^2 H^D(k) \\ = - \int_0^\infty dk k^2 j_0(kr) \hat{h}^D(k). \end{aligned}$$

Using  $\nabla^2 j_0(kr) + k^2 j_0(kr) = 0$  in the integral involving  $k^2 H^D(k)$  gives

$$\nabla^2 H^D(r) = \hat{h}^D(r) \quad (2.8)$$

At this point in the presentation of Wertheim's operator formalism, it should be mentioned that the operator  $D_{op}$  and an associated function  $H^D(r)$  (and also  $C^D(r)$ ) have been introduced (cf. equations (15) and (16) of Wertheim's (1971) paper). As shown by Wertheim (1971), the operators allow the angular convolution over  $\vec{\Omega}_3$  in the Ornstein-Zernike equation to be performed. The resulting Ornstein-Zernike is given in terms of  $\hat{h}^D(r)$  and  $\hat{C}^D(r)$  (or  $\hat{h}^D(k)$  and  $\hat{C}^D(k)$  in  $k$  space) rather than  $h^D(r)$  and  $c^D(r)$ . Thus the relationship between  $\hat{h}^D(r)$ ,  $H^D(r)$  and  $h^D(r)$  must be established in order to apply the original closure rules (given in terms of  $h^D(r)$  and  $c^D(r)$ ) to the new functions  $\hat{h}^D(r)$  and  $\hat{C}^D(r)$  of the reformulated Ornstein-Zernike equation (cf. equations (25) and (29) of Wertheim's (1971) article). Provided the reformulated Ornstein-Zernike equations for  $\hat{h}^D(r)$  and  $\hat{C}^D(r)$  can be solved, the transformation between  $\hat{h}^D(r)$  and  $h^D(r)$  (with  $H^D(r)$  an intermediate step) then allows the radial coefficient  $h^D(r)$  of the pair

distribution function to be determined. It should be noted that greater emphasis has been placed on the D-component of the distribution function rather than the spherical and  $\Delta$  -components. This is due to the angular dependence of the latter components being independent of the  $\vec{r}$  direction. The Fourier and Hankel transforms of these contributions are then determined in terms of  $j_0(kr)$  .

The reformulated Ornstein-Zernike equation in r-space is obtained here through Hankel inversion of the set of coupled equations in k-space. Our convention is to use the zeroth order Hankel inversion of the k dependent equations - equations (13a) and (13b) of Chapter 2. Such a procedure can be performed and the resulting equations are rewritten in Wertheim's notation:

$$h^A(r) - c^A(r) = \frac{\rho}{3} ( 2 \hat{h}^D * \hat{c}^D + h^A * c^A ) \quad (2.9)$$

$$h^D(r) - c^D(r) = \frac{\rho}{3} ( \hat{h}^D * \hat{c}^D + \hat{h}^D * c^A + h^A * \hat{c}^D )$$

where  $h * c \equiv \int d\vec{r}_3 h(r_{13}) c(r_{32})$ .

The important variables in r-space are certainly seen to be  $\hat{h}^D(r)$  and  $h^A(r)$  , rather than  $h^D(r)$  and  $h^A(r)$  . Thus  $\hat{h}^D(r) = \nabla^2 H^D(r)$  is a natural function, being the fundamental quantity in the reformulated Ornstein-Zernike equations above. Since the thermodynamics and boundary conditions are formulated in terms of  $h^D(r)$  and  $c^D(r)$  , a transformation between  $\hat{h}^D(r)$  and  $h^D(r)$  is required to complete the problem. This relationship is given by considering the inverse Hankel transform of  $H^D(K) = -h^D(K)/K^2$  . Then

$$\begin{aligned} H^D(r) &= (2\pi^2)^{-1} \int_0^\infty dK K^2 j_0(Kr) H^D(K) \\ &= \frac{2}{\pi} \int_0^\infty dr_0 r_0^2 h^D(r_0) \int_0^\infty dK j_0(Kr) j_2(Kr_0) \end{aligned}$$

where equation (2.5) has been used to replace  $H^D(k) = -h^D(k)/k^2$ . The integration over  $k$  can be reduced to standard form (Watson, 1966) by defining

$$\begin{aligned} I(r, r_0) &= \int_0^\infty dk \, j_0(kr) j_2(kr_0) \\ &= \frac{\pi}{2(r r_0)^{1/2}} \int_0^\infty dk \, k^{-1} J_{\frac{1}{2}}(kr) J_{\frac{5}{2}}(kr_0) \\ &= \begin{cases} \frac{\pi}{4} \left( \frac{r_0^2 - r^2}{r_0^3} \right) & \text{if } r_0 > r > 0 \\ 0 & \text{otherwise.} \end{cases} \end{aligned}$$

This then leads to

$$H^D(r) = \frac{1}{2} \int_r^\infty dr_0 \, h^D(r_0) (r_0^2 - r^2)/r_0$$

Application of  $\nabla^2$  to this equation gives the required transformation between  $\hat{h}^D(r) = \nabla^2 H^D(r)$  and  $h^D(r)$  as

$$\hat{h}^D(r) = h^D(r) - 3 \int_r^\infty dr_0 \, h^D(r_0)/r_0. \quad (2.10)$$

From the above equations, the D-component of the correlation function is  $h^D(r) D(\vec{r}_1, \vec{r}_2, \vec{r})$  or equivalently

$D_{op}(\vec{r}_1, \vec{r}_2, \vec{r}) H^D(r)$ . This equivalence is not fully appreciated at this point, but this subtle reformulation does allow the angular dependent Ornstein-Zernike equation to be solved in  $r$ -space without Fourier transforming back and forth between  $r$  and  $k$  spaces. Before giving the details of such an approach, an operational form of  $\Delta$ ,

$\Delta_{op}(\vec{r}_1, \vec{r}_2, \vec{r}) H^A(r)$ , is given in order to write  $h$  and  $c$  in terms of the operators  $\Delta_{op}$  and  $D_{op}$ . It can be seen from equation (2.3) and the convention of using the zeroth order Hankel transform throughout that the operator  $\Delta_{op}$  is easily seen to be

$\vec{r}_1(\vec{r}_1) \cdot \vec{r}_2(\vec{r}_2) \nabla^2$ . Alternatively this is given in a

"correspondence principle" that follows from the definition of  $\mathcal{D}_{op}$  in

$$\mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\nabla}) \longleftrightarrow -K^2 \mathcal{D}_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) .$$

Since  $\Delta_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) = \Delta(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) = \vec{s}_1(\vec{\Omega}_1) \cdot \vec{s}_2(\vec{\Omega}_2)$ ,

$$\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\nabla}) \longleftrightarrow -K^2 \vec{s}_1(\vec{\Omega}_1) \cdot \vec{s}_2(\vec{\Omega}_2)$$

and so

$$\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\nabla}) = \vec{s}_1(\vec{\Omega}_1) \cdot \vec{s}_2(\vec{\Omega}_2) \nabla^2 .$$

The above heuristic argument for the form of the operator  $\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\nabla})$  can be made quite rigorous by following the Fourier transform of

$h^\Delta(r) \Delta(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r)$  and subsequent inversion. Since most of the important steps have already been set out in the introduction of the operator  $\mathcal{D}_{op}$ , the Fourier transform of  $h^\Delta(r) \Delta(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r)$  to be inverted is  $\tilde{h}^\Delta(K) \Delta_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)$  where

$$\Delta_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) = \vec{s}_1(\vec{\Omega}_1) \cdot \vec{s}_2(\vec{\Omega}_2)$$

and

$$\tilde{h}^\Delta(K) = 4\pi \int_0^\infty dr r^2 j_0(Kr) h^\Delta(r)$$

The inversion of  $\tilde{h}^\Delta(K) \Delta_K$  is then given by

$$\begin{aligned} \int d\vec{K} e^{-i\vec{K} \cdot \vec{r}} \tilde{h}^\Delta(K) \Delta_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) \\ = \vec{s}_1(\vec{\Omega}_1) \cdot \vec{s}_2(\vec{\Omega}_2) \int_0^\infty dk k^2 \tilde{h}^\Delta(k) \int d\vec{\Omega}_K e^{-i\vec{K} \cdot \vec{r}} \\ = 4\pi \int_0^\infty dk k^2 \tilde{h}^\Delta(k) j_0(kr) \vec{s}_1(\vec{\Omega}_1) \cdot \vec{s}_2(\vec{\Omega}_2) . \end{aligned}$$

At this point, Hankel inversion gives  $\hat{h}^\Delta(r) \vec{s}_1(\vec{\Omega}_1) \cdot \vec{s}_2(\vec{\Omega}_2)$  as expected. However introduction of the function  $H^\Delta(K) = -\tilde{h}^\Delta(K)/K^2$  and use of  $\nabla^2 j_0(Kr) + K^2 j_0(Kr) = 0$  gives the above inversion as

$$\vec{s}_1(\vec{\Omega}_1) \cdot \vec{s}_2(\vec{\Omega}_2) \nabla^2 H^\Delta(r)$$

$$\text{where } H^A(r) = 4\pi \int_0^\infty d\kappa \kappa^2 H^A(\kappa) j_0(\kappa r), \quad (2.11)$$

and it can be shown that

$$h^A(r) = \nabla^2 H^A(r).$$

Obviously the definition of  $\hat{h}^A(r)$  is unnecessary since  $\tilde{h}^A(\kappa)$  is a zeroth order Hankel transform anyhow but it is given for completeness as

$$\hat{h}^A(r) = h^A(r) = \nabla^2 H^A(r). \quad (2.12)$$

This shows that

$$\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) H^A(r) = \Delta(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) h^A(r) \quad (2.13)$$

where  $\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega})$  is defined by

$$\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}) = \vec{S}_1(\vec{\Omega}_1) \cdot \vec{S}_2(\vec{\Omega}_2) \nabla^2. \quad (2.14)$$

With these operators  $\Delta_{op}$  and  $D_{op}$ , the correlation function  $h$  can be written either as

$$h(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = h^s(r) I(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) + h^A(r) \Delta(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) + h^D(r) D(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_r) \quad (2.15)$$

or

$$h(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2) = I_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}) H^s(r) + \Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}) H^A(r) + D_{op}(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}) H^D(r). \quad (2.16)$$

In equation (2.16) the identity operator  $I_{op} = 1$  is trivially introduced and thereby  $h^s(r) = H^s(r)$ . Similar equations can be written down for  $c(\vec{r}_1, \vec{\Omega}_1, \vec{r}_2, \vec{\Omega}_2)$ . As mentioned previously the operational form of the expansion for  $h$  and  $c$  allow the Ornstein-Zernike equation to be solved without recourse to Fourier transforms.

This then facilitates the application of the closure rules (of the Mean Spherical Approximation) which are formulated in  $r$  space anyhow.

If the expansions of the form (2.15) for  $h$  and  $c$  were substituted into the Ornstein-Zernike equation, the angular expansion of the convolution term in the equation is very inconvenient. In particular the angular part of any convolution of a  $D$  term with a

$\Delta$  or  $D$  term is dependent on the orientation of  $\vec{r}_3$  vector in the spatial part of the convolution. This is seen in, for example, the more complicated convolution of  $D$  with itself:

$$\begin{aligned} & \int d\vec{\Omega}_3 D(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_{\vec{r}_3}) D(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_{\vec{r}_{32}}) \\ &= \int d\vec{\Omega}_3 \vec{S}_1(\vec{\Omega}_1) \cdot (3\hat{r}_{13}\hat{r}_{13} - \underline{1}) \cdot \vec{S}_3(\vec{\Omega}_3) \vec{S}_3(\vec{\Omega}_3) \cdot (3\hat{r}_{32}\hat{r}_{32} - \underline{1}) \cdot \vec{S}_2(\vec{\Omega}_2) \\ &= \frac{4\pi}{3} \vec{S}_1(\vec{\Omega}_1) \cdot (3\hat{r}_{13}\hat{r}_{13} - \underline{1}) \cdot (3\hat{r}_{32}\hat{r}_{32} - \underline{1}) \cdot \vec{S}_2(\vec{\Omega}_2) \quad (2.17) \end{aligned}$$

where the result  $\int d\vec{\Omega}_3 \vec{S}_3(\vec{\Omega}_3) \vec{S}_3(\vec{\Omega}_3) = 4\pi \underline{1} / 3$

has been used, and the resultant contraction carried out. This result of the angular part of the convolution over all orientations  $\vec{\Omega}_3$  and positions  $\vec{r}_3$  of molecule 3 is very complicated expression for the spatial part of the convolution i.e., integration over  $\vec{r}_3$ . Steele has shown how to solve a simpler problem by elementary changes of angle variables (Steele, 1963). However the resultant complicated algebra can be avoided if one notices that the above contractions in equation (2.17) can be carried out if the  $\hat{r}_{13}$  and  $\hat{r}_{32}$  directions were replaced by a common vector. This is exactly what happens if the Fourier components  $D_K(\vec{\Omega}_i, \vec{\Omega}_j, \vec{\Omega}_K)$  were convoluted over  $\vec{\Omega}_3$  rather than  $D(\vec{\Omega}_i, \vec{\Omega}_j, \vec{\Omega}_{\vec{r}_{ij}})$ . The convolution over

$\vec{\Omega}_3$  is then simplified to

$$\begin{aligned}
 & \int d\vec{\Omega}_3 D_K(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) D_K(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) \\
 &= \frac{4\pi}{3} \vec{s}_1 \cdot (3\hat{K}\hat{K} - \underline{1}) \cdot (3\hat{K}\hat{K} - \underline{1}) \cdot \vec{s}_2 \\
 &= \frac{4\pi}{3} \vec{s}_1 \cdot (3\hat{K}\hat{K} + \underline{1}) \cdot \vec{s}_2 \\
 &= \frac{4\pi}{3} [D_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) + 2\Delta_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)]
 \end{aligned}$$

where the definitions for  $D_K$  and  $\Delta_K$  have been used to simplify the result. This suggests that a closed form convolution is possible in  $r$  space if the "correspondence principle" indicated previously is employed. In other words, the angular convolution can be carried out in the operator format of Wertheim since the directions in equation (2.17) can be effectively replaced by the directional derivative operator  $\vec{\nabla}_{12}$  (and  $\vec{\nabla}_{32}$ ). These operators give the common vector required in equation (2.17) since  $\vec{\nabla}_{12} \equiv \vec{\nabla}_{32} \equiv -\vec{\nabla}_2$  allows  $\vec{\nabla}_{12}$  to serve the same role played by  $\hat{K}$  above. The direct substitution of the operator form of the expansion of the correlation functions into the convolution over  $\vec{\Omega}_3$  is given in Appendix 1. Needless to say, the same convolution properties prescribed by the "correspondence principle" above are found.

The convolutions over  $\vec{\Omega}_3$  of the remaining products of angular functions are much simpler, at least in  $k$  space. Allied with the "correspondence principle", these results complete the solution of the problem of the convolution part of the Ornstein-Zernike in  $r$  space. In  $k$  space, the convolution properties are

$$\int d\vec{\Omega}_3 I_K(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) I_K(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) = 4\pi I_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)$$

$$\begin{aligned} \int d\vec{\Omega}_3 I_K(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) \Delta_K(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) &= \int d\vec{\Omega}_3 I_K(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) D_K(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) \\ &= 0 \end{aligned}$$

$$\int d\vec{\Omega}_3 \Delta_K(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) \Delta_K(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) = \frac{4\pi}{3} \Delta_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)$$

$$\begin{aligned} \int d\vec{\Omega}_3 \Delta_K(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) D_K(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) &= \vec{S}_1(\vec{\Omega}_1) \cdot \left[ \int d\vec{\Omega}_3 \vec{S}_3(\vec{\Omega}_3) \vec{S}_3(\vec{\Omega}_3) \right] \cdot \\ &\quad \cdot (3 \hat{\vec{K}} \hat{\vec{K}} - \mathcal{U}) \cdot \vec{S}_2(\vec{\Omega}_2) \\ &= \frac{4\pi}{3} D_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) \end{aligned}$$

and from above,

$$\begin{aligned} \int d\vec{\Omega}_3 D_K(\vec{\Omega}_1, \vec{\Omega}_3, \vec{\Omega}_K) D_K(\vec{\Omega}_3, \vec{\Omega}_2, \vec{\Omega}_K) &= \frac{4\pi}{3} [D_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K) \\ &\quad + 2\Delta_K(\vec{\Omega}_1, \vec{\Omega}_2, \vec{\Omega}_K)] . \end{aligned}$$

### Appendix 3

#### The Convolution Properties of I, Δ and D

In this Appendix, the angular convolution of the operators in equation (28) of Chapter 2 will be detailed. The radial dependence of these operators will be omitted for simplicity.

Any convolution involving the identity operator vanishes. This is due to the first of two useful integrals,

$$\int d\vec{\Omega}_3 \vec{S}(\vec{\Omega}_3) = \underline{0} \quad (3.1)$$

and

$$\int d\vec{\Omega}_3 \vec{S}(\vec{\Omega}_3) \vec{S}(\vec{\Omega}_3) = \frac{4\pi}{3} \underline{U} \quad (3.2)$$

where  $\underline{0}$  and  $\underline{U}$  are the 3 x 3 zero and unit tensors, respectively.

All other convolutions can be systematically evaluated. The basic technique will be given here for the most complicated case involving

$D_{op} \cdot D_{op}$  . From the definition of  $D_{op}$  ,

$$D_{op}(\vec{\Omega}_1, \vec{\Omega}_3) = \vec{S}_1(\vec{\Omega}_1) \cdot (3 \vec{\nabla}_{13} \vec{\nabla}_{13} - \underline{U} \nabla_{13}^2) \cdot \vec{S}_3(\vec{\Omega}_3) \quad (3.3)$$

$$D_{op}(\vec{\Omega}_3, \vec{\Omega}_2) = \vec{S}_3(\vec{\Omega}_3) \cdot (3 \vec{\nabla}_{32} \vec{\nabla}_{32} - \underline{U} \nabla_{32}^2) \cdot \vec{S}_2(\vec{\Omega}_2)$$

The use of equation (3.3) simplifies the convolution  $D_{op} \cdot D_{op}$ :

$$\begin{aligned} D_{op}(\vec{\Omega}_1, \vec{\Omega}_3) \cdot D_{op}(\vec{\Omega}_3, \vec{\Omega}_2) &= \vec{S}_1(\vec{\Omega}_1) \cdot (3 \vec{\nabla}_{13} \vec{\nabla}_{13} - \underline{U} \nabla_{13}^2) \cdot \int d\vec{\Omega}_3 \vec{S}_3(\vec{\Omega}_3) \vec{S}_3(\vec{\Omega}_3) \cdot \\ &\quad \times (3 \vec{\nabla}_{32} \vec{\nabla}_{32} - \underline{U} \nabla_{32}^2) \cdot \vec{S}_2(\vec{\Omega}_2) \\ &= \vec{S}_1(\vec{\Omega}_1) \cdot (3 \vec{\nabla}_{13} \vec{\nabla}_{13} - \underline{U} \nabla_{13}^2) \cdot \frac{4\pi}{3} \underline{U} \cdot (3 \vec{\nabla}_{32} \vec{\nabla}_{32} - \underline{U} \nabla_{32}^2) \cdot \vec{S}_2(\vec{\Omega}_2). \end{aligned}$$

Since  $\mathcal{D}_{op}$  operates on functions of  $r$  only this allows the transformation of  $\vec{\nabla}_{13}$  to  $\vec{\nabla}_{12}$  and  $\vec{\nabla}_{32}$  to  $-\vec{\nabla}_{12}$  and the contractions to be done in terms of  $\vec{\nabla}_{12}$ . Then

$$\begin{aligned}
 & \mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_3) \cdot \mathcal{D}_{op}(\vec{\Omega}_3, \vec{\Omega}_2) \\
 &= \frac{4\pi}{3} \vec{s}_1(\vec{\Omega}_1) \cdot (3 \vec{\nabla}_{12} \vec{\nabla}_{12} \nabla_{12}^2 + \nabla_{12}^4) \cdot \vec{s}_2(\vec{\Omega}_2) \\
 &= \frac{4\pi}{3} \nabla_{12}^2 \vec{s}_1(\vec{\Omega}_1) \cdot [ (3 \vec{\nabla}_{12} \vec{\nabla}_{12} - \nabla_{12}^2) + 2 \nabla_{12}^2 ] \cdot \vec{s}_2(\vec{\Omega}_2) \\
 &= \frac{4\pi}{3} ( \mathcal{D}_{op}(\vec{\Omega}_1, \vec{\Omega}_2) + 2 \Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2) ) \nabla_{12}^2 .
 \end{aligned}$$

# Appendix 4

## The Orthogonality Properties of I, Δ and D

The orthogonality relations are again based on equations (3.1) and (3.2) given in Appendix 3. Equation (3.1) can be used to show the following orthogonalities :

$$\begin{aligned} & \iint d\vec{\Omega}_1 d\vec{\Omega}_2 I_{op}(\vec{\Omega}_1, \vec{\Omega}_2) \Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2) \\ &= \iint d\vec{\Omega}_1 d\vec{\Omega}_2 I_{op}(\vec{\Omega}_1, \vec{\Omega}_2) D_{op}(\vec{\Omega}_1, \vec{\Omega}_2) \\ &= 0 . \end{aligned}$$

The  $\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2)$  and  $D_{op}(\vec{\Omega}_1, \vec{\Omega}_2)$  are also orthogonal as follows.

Commutation of the dot product in  $\Delta_{op}(\vec{\Omega}_1, \vec{\Omega}_2)$  in

$$\begin{aligned} & \iint d\vec{\Omega}_1 d\vec{\Omega}_2 (\vec{S}_1(\vec{\Omega}_1) \cdot \vec{S}_2(\vec{\Omega}_2) \nabla^2) \vec{S}_1(\vec{\Omega}_1) \cdot (3 \vec{\nabla} \vec{\nabla} - \nabla^2) \cdot \vec{S}_2(\vec{\Omega}_2) \\ &= \nabla^2 \int d\vec{\Omega}_2 \vec{S}_2(\vec{\Omega}_2) \cdot \int d\vec{\Omega}_1 \vec{S}_1(\vec{\Omega}_1) \vec{S}_1(\vec{\Omega}_1) \cdot (3 \vec{\nabla} \vec{\nabla} - \nabla^2) \cdot \vec{S}_2(\vec{\Omega}_2) \\ &= \frac{4\pi}{3} \nabla^2 (3 \vec{\nabla} \cdot (\int d\vec{\Omega}_2 \vec{S}_2(\vec{\Omega}_2) \vec{S}_2(\vec{\Omega}_2)) \cdot \vec{\nabla} - \nabla^2 \int d\vec{\Omega}_2) \\ &= \frac{4\pi}{3} \nabla^2 (3 \cdot \frac{4\pi}{3} \vec{\nabla} \cdot \vec{\nabla} - 4\pi \nabla^2) \\ &= 0 . \end{aligned}$$

Similar operations on the products  $I_{op} I_{op}$  ,  $\Delta_{op} \Delta_{op}$  and  $D_{op} D_{op}$  give non-vanishing results.

Appendix 5

Uncoupling of Equations (40) and (41) of Chapter 2

Equations (46) can be solved for  $\hat{h}_{\alpha\beta}^D(r)$  and  $\hat{h}_{\alpha\beta}^A(r)$  by inspection to give

$$\hat{h}_{\alpha\beta}^D(r) = 2 (h_{\alpha\beta}^+(r) + \frac{1}{2} h_{\alpha\beta}^-(r)) \quad (5.1)$$

and

$$\hat{h}_{\alpha\beta}^A(r) = 2 (h_{\alpha\beta}^+(r) - h_{\alpha\beta}^-(r)) \quad (5.2)$$

Similar equations can be written down for  $\hat{c}_{\alpha\beta}^D(r)$  and  $\hat{c}_{\alpha\beta}^A(r)$ . When these equations for  $\hat{h}_{\alpha\beta}^D(r)$  and  $\hat{c}_{\alpha\beta}^A(r)$ ,  $\hat{h}_{\alpha\beta}^A(r)$  and  $\hat{c}_{\alpha\beta}^D(r)$  are substituted into equations (40) and (41) of Chapter 2, one obtains

$$h_{\alpha\beta}^+ - h_{\alpha\beta}^- = c_{\alpha\beta}^+ - c_{\alpha\beta}^- + \sum_{\gamma} \rho_{\gamma} (2 h_{\alpha\gamma}^+ * c_{\gamma\beta}^+ + h_{\alpha\gamma}^- * c_{\gamma\beta}^-) \quad (5.3)$$

and

$$2h_{\alpha\beta}^+ + h_{\alpha\beta}^- = 2c_{\alpha\beta}^+ + c_{\alpha\beta}^- + \sum_{\gamma} \rho_{\gamma} (4 h_{\alpha\gamma}^+ * c_{\gamma\beta}^+ - h_{\alpha\gamma}^- * c_{\gamma\beta}^-) \quad (5.4)$$

Linear combinations of 5.3 and 5.4 then give the following independent equations for  $h_{\alpha\beta}^+$  and  $h_{\alpha\beta}^-$ ,

$$h_{\alpha\beta}^+ = c_{\alpha\beta}^+ + \sum_{\gamma} (2\rho_{\gamma}) h_{\alpha\gamma}^+ * c_{\gamma\beta}^+ ,$$

$$h_{\alpha\beta}^- = c_{\alpha\beta}^- + \sum_{\gamma} (-\rho_{\gamma}) h_{\alpha\gamma}^- * c_{\gamma\beta}^- .$$

## Appendix 6

### Solution of Equations (72) and (73) of Chapter 2

Equations (76) and (77) can be obtained from equations (65) and (73) by taking the linear combinations as defined in equations (74) and (75). Multiplying equation (72) by  $R_\alpha$  and adding twice equation (73) gives

$$a_{\alpha\beta} R_\alpha + 2b_{\alpha\beta} = R_\alpha + \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\gamma^3 (a_{\alpha\gamma} R_\alpha + 2b_{\alpha\gamma}). \quad (6.1)$$

Using equation (74) allows this to be rewritten as

$$A_{\alpha\beta} = R_\alpha + \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\gamma^3 A_{\alpha\gamma} \quad (6.2)$$

from which equation (76) can be immediately written down, using

$$\sum_\gamma \delta_{\gamma\beta} A_{\alpha\gamma} = A_{\alpha\beta} \quad . \quad \text{Performing the linear combination}$$

of equations (72) and (73) similarly gives

$$\begin{aligned} & (3R_\alpha + R_\beta) a_{\alpha\beta} + 6b_{\alpha\beta} \\ &= (3R_\alpha + R_\beta) + \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\gamma^2 [(3a_{\alpha\gamma} R_\alpha R_\beta \\ & \quad + a_{\alpha\gamma} R_\gamma R_\beta + 6b_{\alpha\gamma} R_\beta) + (3a_{\alpha\gamma} R_\alpha R_\gamma + 6b_{\alpha\gamma} R_\gamma)]. \end{aligned} \quad (6.3)$$

Using equations (74) and (75) again, this equation can be rewritten in terms of  $A_{\alpha\beta}$  and  $B_{\alpha\beta}$  as

$$B_{\alpha\beta} = (3R_\alpha + R_\beta) + \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\gamma^2 (R_\beta B_{\alpha\gamma} + 3R_\gamma A_{\alpha\gamma})$$

The sum over  $\gamma$  involving  $B_{\alpha\gamma}$  can incorporate the  $B_{\alpha\beta}$  on the left hand side of the above equation by using  $B_{\alpha\beta} = \sum_\gamma \delta_{\gamma\beta} B_{\alpha\gamma}$  .

This then allows equation (6.3) to be rewritten as

$$\begin{aligned} & \sum_\gamma \left( \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\gamma^2 R_\beta - \delta_{\gamma\beta} \right) B_{\alpha\gamma} \\ &= (3R_\alpha + R_\beta) + 3 \sum_\gamma \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\gamma^3 A_{\alpha\gamma} \quad . \end{aligned} \quad (6.4)$$

This is equation (77) in Chapter 2. Equation (62) is to be solved for the  $A_{\alpha\beta}$  which are then used to evaluate the right hand side of equation (64). This procedure allows the  $B_{\alpha\beta}$  to be determined from the  $A_{\alpha\beta}$ . However a different approach is adopted here: equation (73) is solved for the  $b_{\alpha\beta}$  given  $A_{\alpha\beta}$  from equation (6.2), and  $B_{\alpha\beta}$  given from equations (74) and (75).

The explicit details for the solution of equation (6.2) will now be given. For binary mixtures (  $\gamma = 1, 2$  ) equation (6.2) can be written out as two independent sets of linear equations to be solved.

In matrix form,

$$\begin{bmatrix} \frac{\pi}{6} \rho_1^3 R_1^3 - 1 & \frac{\pi}{6} \rho_2^3 R_2^3 & 0 & 0 & A_{11} \\ \frac{\pi}{6} \rho_1^2 R_1^3 & \frac{\pi}{6} \rho_2^2 R_2^3 - 1 & 0 & 0 & A_{12} \\ 0 & 0 & \frac{\pi}{6} \rho_1^2 R_1^3 - 1 & \frac{\pi}{6} \rho_2^2 R_2^3 & A_{21} \\ 0 & 0 & \frac{\pi}{6} \rho_2^2 R_1^3 & \frac{\pi}{6} \rho_1^2 R_2^3 - 1 & A_{22} \end{bmatrix} = - \begin{bmatrix} R_1 \\ R_1 \\ R_2 \\ R_2 \end{bmatrix} \quad (6.5)$$

It is clear that the sets of unknowns  $A_{11}$ ,  $A_{12}$  and  $A_{21}$ ,  $A_{22}$  are independent of each other, reducing the problem to two  $2 \times 2$  matrix inversion operations. From Cramer's rule it can be shown that

$$A_{11} = \frac{R_1 (1 + \frac{\pi}{6} \rho_2 R_2^3 K_{22} (K_{12}^2 / (K_{11} K_{22}) - 1))}{1 + \frac{\pi^2}{36} \rho_1 K_{11} R_1^3 \rho_2 K_{22} R_2^3 (1 - K_{12}^2 / (K_{11} K_{22})) - \frac{\pi}{6} (\rho_1 K_{11} R_1^3 + \rho_2 K_{22} R_2^3)}$$

$$A_{12} = \frac{R_1}{1 + \frac{\pi^2}{36} \rho_1 K_{11} R_1^3 \rho_2 K_{22} R_2^3 (1 - K_{12}^2 / (K_{11} K_{22})) - \frac{\pi}{6} (\rho_1 K_{11} R_1^3 + \rho_2 K_{22} R_2^3)}$$

$$A_{21} = \frac{R_2}{1 + \frac{\pi^2}{36} \rho_1 K_{11} R_1^3 \rho_2 K_{22} R_2^3 (1 - K_{12}^2 / (K_{11} K_{22})) - \frac{\pi}{6} (\rho_1 K_{11} R_1^3 + \rho_2 K_{22} R_2^3)}$$

and

$$A_{22} = \frac{R_2 (1 + \frac{\pi}{6} \rho_1 K_{11} R_1^3 (K_{12}^2 / (K_{11} K_{22}) - 1))}{1 + \frac{\pi^2}{36} \rho_1 K_{11} R_1^3 \rho_2 K_{22} R_2^3 (1 - K_{12}^2 / (K_{11} K_{22})) - \frac{\pi}{6} (\rho_1 K_{11} R_1^3 + \rho_2 K_{22} R_2^3)}$$

These explicit expressions for  $A_{11}$ ,  $A_{12}$ ,  $A_{21}$  and  $A_{22}$  are given in the general formula

$$A_{\alpha\beta} = \frac{R_\alpha (1 + g_3^{\alpha\beta} - g_3^{12})}{1 - g_3^{12} + \Delta} \quad (6.6)$$

where

$$g_3^{\alpha\beta} = \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\gamma^3$$

and

$$\Delta = \frac{\pi^2}{36} \rho_1 K_{11} R_1^3 \rho_2 K_{22} R_2^3 (1 - K_{12}^2 / (K_{11} K_{22})).$$

In order to determine  $B_{\alpha\beta}$ , equation (73) is solved for  $b_{\alpha\beta}$  in terms of the  $A_{\alpha\beta}$  above and  $B_{\alpha\beta}$  is then determined from equations (74) and (75) as

$$B_{\alpha\beta} = 3A_{\alpha\beta} + (A_{\alpha\beta} - 2b_{\alpha\beta})R_\beta/R_\alpha. \quad (6.7)$$

Equation (73) is rewritten in terms of the  $A_{\alpha\beta}$  as

$$b_{\alpha\beta} = \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\gamma^3 b_{\alpha\gamma} - \frac{3}{2} R_\alpha \sum_{\gamma=1}^2 \frac{\pi}{6} \rho_\gamma^{\alpha\beta} R_\gamma^2 A_{\alpha\gamma}. \quad (6.8)$$

Direct substitution of  $\alpha, \beta = 1, 2$  then gives two independent matrix equations. These are

$$\begin{bmatrix} \frac{\pi}{6} \rho_1^{11} R_1^3 - 1 & \frac{\pi}{6} \rho_2^{11} R_2^3 \\ \frac{\pi}{6} \rho_1^{12} R_1^3 & \frac{\pi}{6} \rho_2^{21} R_2^3 - 1 \end{bmatrix} \begin{bmatrix} b_{11} \\ b_{12} \end{bmatrix} = \frac{3R_1}{2} \begin{bmatrix} \frac{\pi}{6} \rho_1^{11} R_1^2 A_{11} + \frac{\pi}{6} \rho_2^{11} R_2^2 A_{12} \\ \frac{\pi}{6} \rho_1^{12} R_1^2 A_{11} + \frac{\pi}{6} \rho_2^{12} R_2^2 A_{12} \end{bmatrix}, \quad (6.9)$$

and

$$\begin{bmatrix} \frac{\pi}{6} \rho_1^{21} R_1^3 - 1 & \frac{\pi}{6} \rho_2^{21} R_2^3 \\ \frac{\pi}{6} \rho_1^{22} R_1^3 & \frac{\pi}{6} \rho_2^{22} R_2^3 - 1 \end{bmatrix} \begin{bmatrix} b_{21} \\ b_{22} \end{bmatrix} = \frac{3R_2}{2} \begin{bmatrix} \frac{\pi}{6} \rho_1^{21} R_1^2 A_{21} + \frac{\pi}{6} \rho_2^{21} R_2^2 A_{22} \\ \frac{\pi}{6} \rho_1^{22} R_1^2 A_{21} + \frac{\pi}{6} \rho_2^{22} R_2^2 A_{22} \end{bmatrix}. \quad (6.10)$$

Application of Cramer's Rule then gives

$$b_{11} = \frac{\frac{3}{2} R_1 (A_{11} R_2 \frac{\pi^2}{36} R_1^2 R_2^2 (\rho_1'' \rho_2'^2 - \rho_2'' \rho_1'^2) - \frac{\pi}{6} \rho_1'' R_1^2 A_{11} - \frac{\pi}{6} \rho_2'' R_2^2 A_{12})}{1 - \xi_3^{12} + \Delta}$$

$$b_{12} = \frac{\frac{3}{2} R_1 (A_{12} R_1 \frac{\pi^2}{36} R_1^2 R_2^2 (\rho_1'' \rho_2'^2 - \rho_2'' \rho_1'^2) - \frac{\pi}{6} \rho_1'^2 R_1^2 A_{11} - \frac{\pi}{6} \rho_2'^2 R_2^2 A_{12})}{1 - \xi_3^{12} + \Delta}$$

$$b_{21} = \frac{\frac{3}{2} R_2 (A_{21} R_2 \frac{\pi^2}{36} R_1^2 R_2^2 (\rho_1^{21} \rho_2^{22} - \rho_1^{22} \rho_2^{21}) - \frac{\pi}{6} \rho_1^{21} R_1^2 A_{21} - \frac{\pi}{6} \rho_2^{21} R_2^2 A_{22})}{1 - \xi_3^{12} + \Delta}$$

$$b_{22} = \frac{\frac{3}{2} R_2 (A_{22} R_1 \frac{\pi^2}{36} R_1^2 R_2^2 (\rho_1^{21} \rho_2^{22} - \rho_1^{22} \rho_2^{21}) - \frac{\pi}{6} \rho_1^{22} R_1^2 A_{21} - \frac{\pi}{6} \rho_2^{22} R_2^2 A_{22})}{1 - \xi_3^{12} + \Delta} \quad (6.11)$$

Study of the equations above leads to the general form of

$$R_\beta b_{\alpha\beta} = \frac{3}{2} R_\alpha \left[ \frac{A_{\alpha\beta} \Delta}{D} - \frac{R_\alpha R_\beta \xi_2^{\alpha\beta}}{D^2} + \frac{\Delta R_\beta}{D^2} \right] \quad (6.12)$$

where  $D = (1 - \xi_3^{12} + \Delta)$  has been introduced. From equations (6.6), (6.7) and (6.12) it then follows that

$$B_{\alpha\beta} = \frac{3R_\alpha + R_\beta}{D} + \frac{3R_\alpha R_\beta \xi_2^{\alpha\beta}}{D^2} + \frac{(3R_\alpha + R_\beta)(\xi_3^{\alpha\beta} - \xi_3^{12})}{D} - \frac{3\Delta(R_\alpha + R_\beta)}{D^2} - \frac{3\Delta R_\alpha(\xi_3^{\alpha\beta} - \xi_3^{12})}{D^2}. \quad (6.13)$$

The first two terms in equation (6.13) are obtained in the equal radii case where  $\Delta=0$  and  $D=(1-\xi_3^{12})$ , and also for the simpler case of hard spheres, studied by Baxter (Baxter, 1970).

### Appendix 7

#### The Dipolar Contribution to the Gibbs Free Energy of a Mixture: $\Delta G = \Delta E$

The dipolar contribution to the internal energy of a mixture is  $\Delta E$  where  $\Delta E$  per unit volume is given by

$$\frac{\Delta E}{V} = \frac{4\pi}{3} \sum_{\alpha, \beta} \sqrt{\rho_{\alpha} \rho_{\beta}} m_{\alpha} m_{\beta} \sqrt{\rho_{\alpha} \rho_{\beta}} K_{\alpha\beta} \quad (7.1)$$

From equations (86) of Chapter 2 and (38) of Chapter 3, it can be seen that  $\sqrt{\rho_{\alpha} \rho_{\beta}} K_{\alpha\beta}$  (under the guise of  $K_n^*$ ,  $K_{12}^*$  and  $\Delta$ ) are functions of  $\beta \sqrt{\rho_{\alpha} \rho_{\beta}} m_{\alpha} m_{\beta}$ . For fixed values of molecular parameters  $R_{\alpha}$  and  $m_{\alpha}$ ,  $\sqrt{\rho_{\alpha} \rho_{\beta}} K_{\alpha\beta}$  and  $\Delta E/V$  are functions of  $(\beta/V, N_1, N_2)$  where  $N_{\alpha}$  is the number of particles of species  $\alpha$  present in the mixture. Such dependence is accentuated in equation (7.2):

$$\frac{\Delta E}{V} = \frac{\Delta E}{V}(N_1, N_2, \beta/V) \quad (7.2)$$

Equation (7.2) is a relationship giving  $\Delta E/V$  as a function of the product of temperature and volume. Such a degeneracy in  $\Delta E$  is conferred on other thermodynamic properties in excess of those of the hard core reference state, among which are  $\Delta A/V$  and  $\Delta p$ . Equation (7.2) is not specific to the excess dipolar properties as developed in the Mean Spherical Approximation but the resulting degeneracy of the excess thermodynamic functions is found generally in solutions of the Mean Spherical Approximation (Wertheim, 1971; Waisman 1973a, b; Waisman and Lebowitz, 1970, 1972a, 1972b). This degeneracy phenomenon is basically attributed to the product of independent variables of the form density x molecular well depth x temperature<sup>-1</sup> entering the self-consistency equations found in the solutions of the Mean Spherical

Approximation. A physical explanation as to why this is so has not been fully appreciated as yet.

The peculiarities of the dependence of  $\Delta E/V$  on  $\beta/V$  are detailed in the derivation of the dipolar contribution to the pressure,  $\Delta p$ . This is given from exact thermodynamic relationships, employing equation (7.2) for  $\Delta E/V$ . Equations (7.3) and (7.4) give the dipolar contributions  $\Delta p$  and  $\Delta A$  in terms of  $\Delta E$ :

$$\Delta p = - \left( \frac{\partial \Delta A}{\partial V} \right)_{N_1, N_2, \beta = 1/(KT)}, \quad (7.3)$$

where

$$\beta \Delta A(N_1, N_2, V, \beta) = \int_0^\beta d\beta' \Delta E(N_1, N_2, V, \beta'). \quad (7.4)$$

Straightforward substitution of equation (7.2) for  $\Delta E$  into equation (7.4) which is then substituted for  $\Delta A$  in equation (7.3) gives

$$-\Delta p = \frac{\partial}{\partial V} \left[ \frac{V}{\beta} \int_0^\beta d\beta' \frac{\Delta E(N_1, N_2, \beta'/V)}{V} \right] \quad (7.5)$$

$$= \frac{\partial}{\partial V} \left[ \frac{V}{\beta} \int_0^{\beta/V} d(\beta'/V) \Delta E(N_1, N_2, \beta'/V) \right]. \quad (7.6)$$

The volume derivative simply gives

$$\begin{aligned} -\Delta p &= \frac{1}{\beta} \int_0^{\beta/V} d(\beta'/V) \Delta E(N_1, N_2, \beta'/V) - \frac{\Delta E}{V}(N_1, N_2, \beta/V) \\ &= \frac{\Delta A}{V} - \frac{\Delta E}{V} \end{aligned} \quad (7.7)$$

where the equation (7.4) is used to obtain the second equality.

Rewriting equation (7.7) simply gives

$$\Delta p = \frac{\Delta E}{V} - \frac{\Delta A}{V}. \quad (7.8)$$

In comparison to the excess thermodynamic properties (excess being over the reference state of a hard core fluid) as given by equations (1) - (5) of Chapter 3, where the equality

$$\Delta G = \Delta A + V \Delta p$$

has been given, it follows that, within the Mean Spherical Approximation,

$$\Delta G = \Delta E . \quad (7.9)$$

Other thermodynamic peculiarities of the Mean Spherical Approximation have been given by Rushbrooke et al. (1973).

## Appendix 8

### Excess Gibbs Free Energies for a Mixture

For a mixture of any two species characterized by  $N_1$  ,  $N_2$  ,  $p$  , and  $T$ , the excess Gibbs free energy,  $G_{\text{mixt}}^{\text{ex}}(N_1, N_2, p, T)$  of the real mixture over a mixture of ideal gases of the same number and type of molecules, pressure and temperature is

$$G_{\text{mixt}}^{\text{ex}}(N_1, N_2, p, T) = G_{\text{mixt}}(N_1, N_2, p, T) - G_{\text{mixt}}^{\text{ideal}}(N_1, N_2, p, T). \quad (8.1)$$

Similarly, the Gibbs free energy of the pure component  $\alpha$  , in excess of that of an ideal gas with the same number of molecules  $N_\alpha$  and under the same conditions of pressure and temperature is

$$G_{\text{pure}, \alpha}^{\text{ex}}(N_\alpha, p, T) = G_{\text{pure}, \alpha}(N_\alpha, p, T) - G_{\text{pure}, \alpha}^{\text{ideal}}(N_\alpha, p, T). \quad (8.2)$$

In the above equations,  $G_{\text{pure}, \alpha}(N_\alpha, p, T)$  and  $G_{\text{mixt}}(N_1, N_2, p, T)$  are the Gibbs free energies of the pure unmixed component  $\alpha$  and the mixture, respectively.

A further property which proves most useful in studying thermodynamics of mixtures is that of the change in the Gibbs free energy on mixing. This gives the difference between the Gibbs free energies of the mixture and that of the sum of the separate pure components before mixing. The Gibbs free energy of mixing is denoted here by  $\Delta G$  and is defined in equation (8.3):

$$\Delta G(N_1, N_2, p, T) = G_{\text{mixt}}(N_1, N_2, p, T) - \sum_{\alpha} x_{\alpha} G_{\text{pure}, \alpha}(N_{\alpha}, p, T), \quad (8.3)$$

where  $x_{\alpha}$  is the mole fraction of component  $\alpha$  in the mixture.

$\Delta G$  can also be expressed in terms of the more useful excess properties defined in equations (8.1) and (8.2). For a mixture of ideal gases,  $\Delta G$  is simply  $NKT \sum_{\alpha} x_{\alpha} \ln x_{\alpha}$  (Hill, 1964). This is used to simplify the following ideal term of mixing,

$$\begin{aligned} \Delta G^{\text{ideal}}(N_1, N_2, p, T) &= G_{\text{mixt}}^{\text{ideal}}(N_1, N_2, p, T) - \sum_{\alpha} x_{\alpha} G_{\text{pure}, \alpha}^{\text{ideal}}(N_{\alpha}, p, T) \\ &= NKT \sum_{\alpha} x_{\alpha} \ln x_{\alpha}, \end{aligned} \quad (8.4)$$

where  $N$  is the total number of molecules,  $N_1 + N_2$ . In terms of the excess Gibbs free energies, the change in the free energy of mixing is then

$$\begin{aligned} \Delta G &= G_{\text{mixt}}^{\text{ex}}(N_1, N_2, p, T) - \sum_{\alpha} x_{\alpha} G_{\text{pure}, \alpha}^{\text{ex}}(N_{\alpha}, p, T) \\ &\quad + NKT \sum_{\alpha} x_{\alpha} \ln x_{\alpha}. \end{aligned} \quad (8.5)$$

The criterion of diffusional stability is usually given as (Rowlinson, 1971)

$$\left( \frac{\partial^2 G_{\text{mixt}}}{\partial x^2} \right)_{p, T} > 0. \quad (8.6)$$

However, it can be shown that  $\Delta G(N_1, N_2, p, T)$ , and not  $\Delta G_{\text{mixt}}^{\text{ex}}(N_1, N_2, p, T)$ , has the same curvature as  $G_{\text{mixt}}(N_1, N_2, p, T)$ . This is given in the following:

$$\left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{p, T} = \left( \frac{\partial^2 G_{\text{mixt}}}{\partial x^2} \right)_{p, T}. \quad (8.7)$$

Fortunately, equation (8.7) permits the calculable  $\Delta G(N_1, N_2, p, T)$  to be used in the diffusional stability criterion in place of

$G_{\text{mixt}}(N_1, N_2, p, T)$ . More importantly,  $\Delta G$  only differs by a linear term in  $x$ , at the most, from  $G_{\text{mixt}}$ . Thus the application of the common tangent construction of Chapter 3 to

$G_{\text{mixt}}$  applies equally well to  $\Delta G$ : the additional constant term is defined at both composition values to have the same slope.

Returning to equation (8.5), we can define a further excess Gibbs free energy, denoted by  $G^E(N_1, N_2, p, T)$ , as the difference between the free energy of mixing for the real mixture and that of the ideal mixture, at the same conditions of  $N_1$ ,  $N_2$ ,  $p$  and  $T$ . The definition of  $G^E$  in terms of  $\Delta G$  and  $\Delta G^{\text{ideal}}$  and the substitution of equations (8.4) and (8.5) for these quantities leads to an expression for  $G^E$  in terms of the appropriate Gibbs free energies minus the corresponding ideal gas terms:

$$\begin{aligned} G^E(N_1, N_2, p, T) &= \Delta G(N_1, N_2, p, T) - \Delta G^{\text{ideal}}(N_1, N_2, p, T) \\ &= G_{\text{mixt}}^{\text{ex}}(N_1, N_2, p, T) - \sum_{\alpha} x_{\alpha} G_{\text{pure}, \alpha}^{\text{ex}}(N_{\alpha}, p, T). \end{aligned} \quad (8.8)$$

From equations (8.6) - (8.8),  $G^E$  and  $\Delta G$  are simply related by the entropic term of ideal mixing, viz.,

$$\Delta G = G^E + NKT \sum_{\alpha} x_{\alpha} \ln x_{\alpha}. \quad (8.9)$$

The above equations were developed by Neff and McQuarrie (1975).

Unfortunately, only one of  $G_{\text{mixt}}^{\text{ex}}$ ,  $\Delta G$  and  $G^E$  can be used in the common tangent construction and stability criteria: the choice being

$\Delta G$ . The Gibbs free energy of the mixture as defined in

equation (8.1) is in excess of the ideal mixture property and so contains the nonlinear entropic " $x \ln x$ " term which is undesirable for the common tangent construction. The change in free energies

$\Delta G$  and  $G^E$  as defined here in equations (8.3) and the first equality in equation (8.8), respectively, are identical to the quantities  $G^M$  and  $G^E$  in the treatment of the thermodynamics of mixtures of Henderson and Leonard (1971). However no relative ideal gas terms are subtracted within their formalism which concentrates on the criterion that  $G^E > NKT/2$  is an indication that phase separation may occur at the values of  $p$ ,  $T$  and  $x$  being considered.

An excess Gibbs free energy for the mixture over some ideal gas state can be defined such that it can be used in the stability criteria (c.f. equation (8.7)) and, more importantly, from the view of coexisting phases when phase separation has taken place (i.e., the stability criteria is violated) can be used in the common tangent construction to obtain the equilibrium compositions of the coexisting phases. The motivation for this new excess free energy can be taken from the equation (8.3) defining the Gibbs free energy of mixing,  $\Delta G$ . Equation (8.3) can be rewritten as

$$\begin{aligned} \Delta G &= G_{\text{mixt}}(N_1, N_2, p, T) - \sum_{\alpha} x_{\alpha} G_{\text{pure}, \alpha}(N_{\alpha}, p, T) \\ &= \left[ G_{\text{mixt}}(N_1, N_2, p, T) - \sum_{\alpha} x_{\alpha} G_{\text{pure}, \alpha}^{\text{ideal}}(N_{\alpha}, p, T) \right] \\ &\quad - \sum_{\alpha} x_{\alpha} G_{\text{pure}, \alpha}^{\text{ex}}(N_{\alpha}, p, T) \quad (8.10) \end{aligned}$$

where  $\sum_{\alpha} x_{\alpha} G_{\text{pure},\alpha}^{\text{ideal}}$  has been added and subtracted to the right hand side of equation (8.3). The terms in square brackets are now identified as the Gibbs free energy of the mixture in excess of that of the unmixed ideal gas components containing the same numbers of molecules  $N_{\alpha}$  at the same  $p$  and  $T$ . This defines the quantity  $G_{\text{mixt}}^{\text{ex}*}(N_1, N_2, p, T)$  which is now given by

$$\begin{aligned} G_{\text{mixt}}^{\text{ex}*}(N_1, N_2, p, T) \\ = G_{\text{mixt}}(N_1, N_2, p, T) - \sum_{\alpha} x_{\alpha} G_{\text{pure},\alpha}^{\text{ideal}}(N_{\alpha}, p, T) \end{aligned} \quad (8.11)$$

In terms of  $G_{\text{mixt}}^{\text{ex}*}$ , the excess properties  $G_{\text{mixt}}^{\text{ex}}$ ,  $\Delta G$  and  $G^E$  are now given by

$$G_{\text{mixt}}^{\text{ex}} = G_{\text{mixt}}^{\text{ex}*} - NKT \sum_{\alpha} x_{\alpha} \ln x_{\alpha} \quad , \quad (8.12)$$

$$\Delta G = G_{\text{mixt}}^{\text{ex}*} - \sum_{\alpha} x_{\alpha} G_{\text{pure},\alpha}^{\text{ex}} \quad , \quad (8.13)$$

and

$$\begin{aligned} G^E = G_{\text{mixt}}^{\text{ex}*} - \sum_{\alpha} x_{\alpha} G_{\text{pure},\alpha}^{\text{ex}} \\ - NKT \sum_{\alpha} x_{\alpha} \ln x_{\alpha} \quad . \end{aligned} \quad (8.14)$$

In the above equations the arguments  $N_1$ ,  $N_2$ ,  $p$  and  $T$  for the mixture and  $N_{\alpha}$ ,  $p$  and  $T$  for the pure functions have been omitted. van Konynenburg (1968) has introduced a similar unmixed ideal gas reference state but at a different pressure than that of the mixture.

Several other authors (Rowlinson, 1971, Guggenheim, 1967) have formulated Gibbs free energies of mixing and their associated excess quantities over the ideal mixing quantity in terms of chemical potentials and activity coefficients. According to Rowlinson (1971), the chemical potential of the  $\alpha^{\text{th}}$  species in a mixture at conditions of constant  $p$  and  $T$ , and composition  $x = N_2 / (N_1 + N_2)$ , is

$\mu_\alpha(p, T, x)$  where

$$\mu_\alpha(p, T, x) = \mu_\alpha^\circ(p, T) + NkT \ln [x_\alpha \gamma_\alpha(p, T, x_\alpha)] \quad (8.15)$$

In equation (8.15),  $\mu_\alpha^\circ(p, T)$  is the chemical potential of pure species  $\alpha$  at the same  $p$  and  $T$  as the mixture;  $\gamma_\alpha(p, T, x_\alpha)$  is the activity coefficient measuring the nonideality of species  $\alpha$  in the mixture, i.e.,  $\gamma_\alpha$  essentially is defined as the excess property over the corresponding species  $\alpha$  if the mixture were ideally behaved, where  $\gamma_\alpha$  is unity. In terms of  $\gamma_\alpha(p, T, x_\alpha)$ , the quantities  $\Delta G$  and  $G^E$  (designated  $G_p^m$  and  $G^E$  in Rowlinson's notation) are given by

$$\begin{aligned} \Delta G &= \sum_\alpha N_\alpha [\mu_\alpha(p, T, x_\alpha) - \mu_\alpha^\circ(p, T)] \\ &= NkT \sum_\alpha x_\alpha \ln [x_\alpha \gamma_\alpha(p, T, x_\alpha)] \end{aligned} \quad (8.16)$$

and

$$G^E = NkT \sum_\alpha x_\alpha \ln \gamma_\alpha(p, T, x_\alpha) \quad (8.17)$$

Guggenheim (1967) has employed the absolute activities  $\lambda_\alpha(p, T, x_\alpha) \exp[\beta \mu_\alpha(p, T, x_\alpha)]$  to formally obtain  $\Delta G$  and  $G^E$  ( $\Delta G_m$  and  $G_m^E$  in his notation) as

$$\Delta G = NkT \sum_\alpha x_\alpha \ln [\lambda_\alpha(p, T, x_\alpha) / \lambda_\alpha^\circ(p, T)] \quad (8.18)$$

and

$$G^E = NKT \sum_{\alpha} x_{\alpha} \ln [ \lambda_{\alpha}(p, T, x_{\alpha}) / (x_{\alpha} \lambda_{\alpha}^{\circ}(p, T)) ] \quad (8.19)$$

In equations (8.18) and (8.19),  $\lambda_{\alpha}^{\circ}(p, T)$  is the absolute activity of pure species  $\alpha$  at the same  $p$  and  $T$  as those of the mixture being considered. The absolute activities  $\lambda_{\alpha}(p, T, x_{\alpha})$  of Guggenheim (1967) and the activity coefficients  $\gamma_{\alpha}(p, T, x_{\alpha})$  of Rowlinson (1971) are related by

$$\gamma_{\alpha}(p, T, x_{\alpha}) = \frac{\lambda_{\alpha}(p, T, x_{\alpha})}{x_{\alpha} \lambda_{\alpha}^{\circ}(p, T)} \quad (8.20)$$

Appendix 9Listings of Computer Programs

This Appendix presents the listings of the computer programs and subroutines used to calculate the excess Gibbs free energies GXS and GMIXT. The listings of COMTAN, which are involved in the common tangent construction, are also included.

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0001      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0002      DIMENSION CP(101),GMIX(101),GPURE(101),GXS(101),FX(101)
           I,TOL(101),DEN(101)
0003      COMMON/DATA1/ SI,W,XM,RW,DW
0004      COMMON/DATA2/ F(5),D(2),X
0005      COMMON/DATA3/ ENERGY(200),BETA(200)
0006      COMMON/DATA4/ P2,P5,Y,IFLAG,DNEW
0007      COMMON/DATA5/SO,BB,FM,I1,D1,M,NPTS,NINTRP,DTW
0008      COMMON/DATA6/BIGG,PTRIAL
0009      COMMON/DATA7/E3,E2
0010      COMMON/DATA8/YO,YIO
0011      COMMON/DATA9/PDIFF
0012      COMMON/DATA10/YB(4)
           C      RHO IS VOLUME DENSITY PI*RHO(I)*R(I)**3/6 ,I=1 TO 2
           C      FM IS MOLE FRACTION OF COMPONENT 2
0013      LOGICAL*1 A(9)
0014      TO=SECONDS(0.)
0015      CALL ASSIGN(6,'TT:')
0016      TYPE 500
0017  500   FORMAT('ENTER DATA FILE ')
0018      CALL ASSIGN(1,,-1)
0019      TYPE 77
0020  77    FORMAT('ENTER LIST FILE ')
0021      CALL ASSIGN(5,,-1)
0022      TYPE 78
0023  78    FORMAT('ENTER OUTPUT FILE ')
0024      CALL ASSIGN(2,,-1)
0025      PI=3.1415926535D0
0026      READ(1,200)W,XM,RHO
0027      RW=1.D0/W
0028      DW=1.D0/(W*DSQRT(W))
0029  200   FORMAT(3F8.4)
0030  130   FORMAT('1X,DENSITY=',F8.3,'RATIO
           1 OF DIPOLES=',F5.2,'RATIO OF RADII=',F5.3)
0031      DI=.001D0
0032      READ(1,155)M,NINTRP,NPTS
0033      IF(M.EQ.0)CALL EXIT
0035      READ(1,190)PMIX1
0036  190   FORMAT(F9.6)
0037      READ(1,165)TEMP
0038      NCT=1
0039  5      IF(TEMP.EQ.0.D0)CALL EXIT
0041      BB=1.D0/TEMP
0042      DTW=BB/NPTS
0043      SO=XM/W**3
0044      FM=0.D0
0045      SI=FM*XM**2/(1.D0-FM)
0046      X=1.D0-8.D0*(W/(1.D0+W))**3
0047      D(2)=0.D0
0048      BO=8.D0*BB
0049      BI=BO*SO*XM
0050      FM=1.D0
0051      GIO=GIBBS(E1,PMIX1,RHO)
0052      FM=0.D0
0053      GO=GIBBS(EO,PMIX1,RHO)
0054      DO 1 I=1,25
0055      FM=(I-1)/25.D0

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0056      SI=FM*XM*XM/(I.D0-FM)
0057      IF(I.LT.3)GO TO 80
0059      RHO=2.D0*DEN(I-1)-DEN(I-2)
0060  80    CALL GFIXIT(PMIX1,RHO,GMIXT,PMIX2)
0061      TOL(I)=FDIFF
0062      IF(TOL(I).LT.1.D-08)GO TO 90
0064      DEN(I)=I.D0
0065      GMIX(I)=0.D0
0066      GO TO 91
0067  90    DEN(I)=RHO
0068      GMIX(I)=GMIXT
0069  91    GPURE(I)=(1.D0-FM)*G0+FM*G10
0070      IF(FM.EQ.0.D0.OR.FM.EQ.1.D0)GO TO 7
0072      GIDEAL=FM*DLOG(FM)+(1.D0-FM)*DLOG((1.D0-FM))
0073      GO TO 8
0074  7     GIDEAL=0.D0
0075  8     GXS(I)=GMIX(I)-GPURE(I)+GIDEAL
0076      GMIX(I)=GMIX(I)+GIDEAL
0077      CP(I)=PMIX2
0078      FX(I)=FM
0079  1     CONTINUE
0080      250  FORMAT(1X,F5.2,3F14.6)
0081      251  FORMAT(1X,F5.2,3F14.6,E16.7)
0082      20    CALL DATE(A)
0083      TTM=SECNDS(TO)/60.D0
0084      IF(NCT.EQ.1)WRITE(5,166) A
0086      IF(NCT.EQ.1)WRITE(5,120)NPTS,DTW
0088  120    FORMAT(1X,I3,'POINTS AT INTERVALS OF ',F6.3)
0089  125    FORMAT(1X,I3,'POINT QUAD ',I3,'POINTS FOR INTERP GIVEN ',I3)
0090      IF(NCT.EQ.1)WRITE(5,130)RHO,XM,W
0092  145    FORMAT('ENTER M,NINTRP ')
0093  155    FORMAT(3I4)
0094  160    FORMAT('ENTER TEMP ')
0095  165    FORMAT(F8.4)
0096      WRITE(5,125)M,NINTRP,NPTS
0097      WRITE(5,195)TEMP,PMIX1
0098  195    FORMAT(1X,'TEMP=',F8.4,' ET PRESSURE=',F9.6)
0099      IF(NCT.EQ.1)WRITE(5,110)
0101  110    FORMAT(3X,'X',3X,'DENSITY',5X,'GMIXTURE',5X,'GMIXING')
0102      WRITE(5,250)O.,Y0,G0,0.
0103      WRITE(5,199)TTM
0104  199    FORMAT(1X,'TIME TAKEN WAS',F8.2,'MINS')
0105      DO 300 I=1,25
0106      IF(TOL(I).LT.1.D-08)GO TO 288
0108      WRITE(5,240)TOL(I)
0109  240    FORMAT(1X,'NO SOLUTION FOUND WITH TOL=',E14.6)
0110      GO TO 300
0111  288    WRITE(5,251)FX(I),DEN(I),GMIX(I),GXS(I),TOL(I)
0112  300    CONTINUE
0113      WRITE(2,222)XM,W,TEMP,PMIX1
0114  222    FORMAT(1X,F6.3,F6.3,F9.6,F9.6)
0115      DO 700 I=1,25
0116  700    WRITE(2,252)FX(I),GMIX(I),GXS(I)
0117      WRITE(2,252)1.0,G10,0.
0118  252    FORMAT(1X,F5.2,2F14.6)
0119      WRITE(5,250)1.0,Y10,G10,0.
0120      READ(I,165)TEMP

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0121      TO=SECNDS(0.)
0122      NCT=NCT+1
0123      GO TO 5
0124  166    FORMAT(1X,9A1)
0125      CALL EXIT
0126      END

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0001      FUNCTION PMIX(RHO)
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      DIMENSION C(3),S(3),T(2),B(2)
0004      COMMON/DATA1/ S1,W,XM
0005      COMMON/DATA2/ F(5),D(2),X
0006      COMMON/DATA3/ ENERGY(200),BETA(200)
0007      COMMON/DATA4/ P2,Y
0008      COMMON/DATA5/ S0,BB,FM,I1,DI,M,NPTS,NINTRP,DTW
0009      COMMON/DATA6/BIGG,PTRIAL
0010      COMMON/DATA10/YB(4)
0011      IF(FM.NE.1.D0)GO TO 6
0013      T(1)=0.D0
0014      GO TO 5
0015 6      T(1)=(1.D0-FM)*RHO/(1.D0-FM+FM*W**3)
0016 5      T(2)=RHO-T(1)
0017      BETA(1)=0.D0
0018      ENERGY(1)=0.D0
0019      DO=0.D0
0020      DO 4 J=1,2
0021      D(1)=DI*J
0022      CALL FIX
0023      B(J)=D(1)*F(1)/(8.D0*T(1))
0024 4      CONTINUE
0025      DI=2.D0*DI+DI*(DTW-B(2))/(B(2)-B(1))
0026      C      WRITE(5,215)B(1),B(2),DI
0027      215      FORMAT(3F16.8)
0028      NT=0
0029      NPTS1=NPTS+5
0030      DO 10 I=2,NPTS1
0031      IF(I.EQ.2)GO TO 80
0032      D(1)=D2
0033      GO TO 90
0034 80      D(1)=DI
0035 90      CALL FIX
0036      IF(1SWICH(2).EQ.1)WRITE(5,180)D(2),F(5),X,F(4)
0038 180      FORMAT(1X,4D14.6)
0039 185      FORMAT(1X,5D14.6)
0040 150      FORMAT(7D14.6)
0041 135      FORMAT(1X,13,2D14.6)
0042      IF(T(1).GT.0D0)GO TO 20
0044      S(1)=0.D0
0045      GO TO 30
0046 20      S(1)=D(1)*F(1)/T(1)
0047 30      IF(T(2).GT.0D0)GO TO 40
0049      S(2)=0.D0
0050      GO TO 50
0051 40      S(2)=D(2)*F(2)/T(2)
0052 50      C(1)=S(1)/F(1)
0053      C(2)=S(2)/F(2)
0054      C(3)=DSQRT(C(1)*C(2)*(1.D0-X))
0055      IF(1SWICH(4).EQ.1)WRITE(5,150)D(1),D(2),S(1),S(2),C(1),C(2),C(3)
0057      ENERGY(I)=T(1)*D(1)+S0*S0*T(2)*D(2)+2.D0*S0*T(1)*T(2)*C(3)
0058      DI2=D(1)+D(2)
0059      BI2=S(1)/8.D0
0060      IF(DI2.GE.0.5D0)WRITE(5,190)DI2,FM,BI2
0062 190      FORMAT(1X,'D(1)+D(2)=',F8.4,'FOR X=',F5.2,'AND BB=',F8.3)
0063      BETA(1)=S(1)/8.D0

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      C      IF(NT.EQ.1)GO TO 300
0064      C      IF(T(1).EQ.0D0)BETA(I)=S(2)/(8.D0*S0*XM)
      C      IF(BETA(I).GT.BETA(I-1))GO TO 22
      C      XX=ENERGY(I-1)
      C      YY=ENERGY(I)
      C      ENERGY(I)=XX
      C      ENERGY(I-1)=YY
      C      XX=BETA(I-1)
      C      YY=BETA(I)
      C      BETA(I)=XX
      C      BETA(I-1)=YY
      C      DTMP1=D1
      C      D1=D0
      C      D0=DTMP1
0066 22      TW=I*DTW
0067      IF(I.GT.2)GO TO 24
0069      DZ=D1+(D1-D0)*(TW-BETA(I))/(BETA(I)-BETA(I-1))
      C      WRITE(5,121)I,D0,D1,DZ
0070 121      FORMAT(IX,I3,3F9.6)
0071      GO TO 10
0072 24      I3=I-3
0073 23      DO 55 J=1,3
0074 55      YB(J)=BETA(I3+J)
0075      YB(4)=TW
      C      WRITE(5,121)I,D0,D1,DZ
0076      CALL POLYFT(D0,D1,D2,X1)
0077      D0=D1
0078      D1=D2
0079      DZ=X1
0080 10      CONTINUE
      C      IF(NT.EQ.1)GO TO 300
      C      D0=0.D0
      C      D1=DTMP
      C      NT=1
      C      GO TO 88
0081 300      IF(ISWICH(9).EQ.1)WRITE(5,135)(J,BETA(J),ENERGY(J),J=1,NPTS1)
0083      CALL STATE(FM,RHO,PE,GE)
0084      FREE=SUM(0.D0,BB,M,NPTRS,NINTRP)
0085      DELTAG=-SEX(NINTRP,NPTS1,BETA,ENERGY,BB)
0086      DELTAP=FREE+DELTAG
0087      PMIX=DELTAP+PE/(8.D0*BB)
0088      G1=8.D0*BB*DELTAG*(1.D0-FM+FM*W*W*W)/RHO
0089      BIGG=G1+GE
0090      IF(ISWICH(15).EQ.1)WRITE(5,185)FM,G1,GE,BIGG,PMIX
0092      RETURN
0093      END

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0001      SUBROUTINE GFIXIT(PMIX1,RHO,GMIXT,PMIX2)
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      COMMON/DATA1/S1,W,XM,RW,DW
0004      COMMON/DATA7/E3,E2
0005      COMMON/DATA4/P0,P5,Y
0006      COMMON/DATA5/ S0,BB,FM,I1,DI,M,NPTS,NINTRP,DTW
0007      COMMON/DATA6/BIGG,PTRIAL
0008      COMMON/DATA8/Y0,Y10
0009      COMMON/DATA9/PDIFF
0010      ALPHA=.05
0011      TOL=1.D-08
0012      T1=SECNDS(0.)
0013      IF(FM.EQ.0.D0)D=Y
0015      I=1
0016      J=1
0017      MM=1
0018      D2=CHANGE(D,PMIX1)/Z.D0**(MM-1)
0019      IF(J.GT.6)GO TO 43
0021      IF(DABS(D2/D).LT.ALPHA)GO TO 15
0023      MM=MM+1
0024      GO TO 5
0025      43      D2=1.D-02
0026      D=.8
0027      45      ISPY=0
0028      P2=PMIX(D)-PMIX1
0029      DO 50 K=1,3,2
0030      DCH=D+(K-2)*D2
0031      P1=PMIX(DCH)-PMIX1
0032      IF(DABS(P1).GT.DABS(P2))GO TO 50
0034      ISPY=1
0035      P2=P1
0036      DNEW=DCH
0037      50      CONTINUE
0038      IF(ISPY.GT.0)GO TO 55
0040      D2=D2/Z.D0
0041      GO TO 45
0042      55      D=DNEW
0043      IF(ISWICH(10).EQ.1)WRITE(5,191)D2,D,P2
0045      191      FORMAT(2F14.6,D16.7)
0046      PDIFF=P2
0047      IF(DABS(D2).LT.TOL)GO TO 25
0049      GO TO 45
0050      15      D=D+D2
0051      20      P2=PMIX(D)-PMIX1
0052      Y4=CHANGE(D,PMIX1)
0053      IF(ISWICH(10).EQ.1)WRITE(5,100)D2,D,E2,E3,P2,J,MM
0055      100      FORMAT(5F14.6,2I4)
0056      J=J+1
0057      PDIFF=P2
0058      IF(SECNDS(T1).LT.500.)GO TO 67
0060      IF(I.EQ.1)GO TO 40
0062      I=I+1
0063      IF(I.EQ.4)GO TO 35
0065      RW=1.D0/RW
0066      DW=-DW
0067      S0=1.D0/S0
0068      S1=1.D0/S1

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0069      FM=1. D0-FM
0070      W=1. D0/W
0071      PMIX1=PMIX1*S0*S0
0072      BB=BB/(S0*S0)
0073      I1=10*(BB+1)
0074      DTW=DTW/(S0*S0)
0075      D=Y10
0076      T1=SECNDS(0.)
0077      IF(I.EQ.3)GO TO 2
0079  40    I=I+1
0080      D=D*MAX1(Y0,Y10)
0081      T1=SECNDS(0.)
0082      GO TO 2
0083  67    IF(DABS(P2).LT.TOL)GO TO 25
0085      IF(J.LT.31)GO TO 1
0087      D=Y10
0088      ALPHA=ALPHA/2. D0
0089      I=I+1
0090      IF(I.LT.5)GO TO 2
0092  35    WRITE(5,110)BB,FM,P2
0093  110    FORMAT(1X,'BETA=',F6.3,'X=',F6.3,'TOL=',D14.6)
0094  25    PMIX2=PMIX1+P2
0095      DZ=CHANGE(D,PMIX1)
0096      IF(E3.GT.0. D0)GO TO 26
0098      WRITE(5,27)FM,BB,D
0099  27    FORMAT(1X,'METASTABLE ROOT AT X=',F5.2,'BETA =',F9.3,'RHO=',F9.6)
0100  26    IF(I.LT.3)GO TO 30
0102      FM=1. D0-FM
0103      RW=1. D0/RW
0104      DW=-DW
0105      S0=1. D0/S0
0106      S1=1. D0/S1
0107      W=1. D0/W
0108      PMIX1=PMIX1*S0*S0
0109      BB=BB/(S0*S0)
0110      I1=10*(BB+1)
0111      DTW=DTW/(S0*S0)
0112  30    RHO1=D/((1. D0-FM+FM*W*W*W)
0113      RHO=D
0114      ZPMIX=PMIX1*8. D0*BB/RHO1
0115      DZPMIX=DLOG(ZPMIX)
0116      GMIXT=BIGG-DLOG(ZPMIX)
0117      IF(ISWICH(14).EQ.1)WRITE(5,200)GMIXT,BIGG,DZPMIX,D
0119  200    FORMAT(1X,D16.8,2D14.6,D16.8)
0120      RETURN
0121      END

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```
0001 SUBROUTINE FIX
0002 IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003 COMMON /DATA1/ S1,W
0004 COMMON /DATA2/ F(5),D(2),X
0005 M=0
0006 CALL WORK
0007 D(2)=D(1)*S1*F(1)/F(2)
0008 5 N=0
0009 30 CALL WORK
0010 X=1. D=F(1)*F(2)/F(3)/F(3)
0011 N=N+1
0012 IF(ISWICH(2).EQ.1)WRITE(5,160)M,N,D(2),X,F(4)
0014 160 FORMAT(1X,2I3,2(D14.6,D14.6))
0015 IF(DABS(F(4)).LE.1.D-06.OR.N.GT.10) GO TO 20
0017 GO TO 30
0018 20 IF(ISWICH(1).EQ.1)WRITE(5,180)M,N,D(2),F(5),X,F(4)
0020 180 FORMAT(1X,2I3,2(D14.6,D14.6))
0021 D(2)=D(1)*S1*F(1)/F(2)
0022 M=M+1
0023 170 FORMAT(1X,2(I3,D14.6,D14.6))
0024 IF(DABS(F(5)).LE.1.D-06.OR.M.GT.10) GO TO 10
0026 GO TO 5
0027 10 IF(ISWICH(0).EQ.1)WRITE(5,170)M,D(2),F(5),N,X,F(4)
0029 RETURN
0030 END
```

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```

0001      FUNCTION SEX(NINTRP,NPTS,X,Y,XX)
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      DIMENSION X(1),Y(1)
0004      IF(NINTRP.LT.3.OR.NPTS.LT.NINTRP)STOP
0005      NPTSI=NPTS-1
0007      DO3 I=1,NPTSI
0008      IF(XX.LT.X(I))GO TO 4
0010  3      CONTINUE
0011      NFIN=NPTS
0012  10     NST=NPTS-NINTRP+1
0013      GO TO 7
0014  4      IF(I.NE.1)GO TO 9
0015      NST=1
0017  5      NFIN=NINTRP
0018      GO TO 7
0019  9      IF(I.LT.NPTS-1)GO TO 11
0021      NST=NPTS-NINTRP+1
0022      NFIN=NPTS
0023      GO TO 7
0024  11     NST=1
0025      NFIN=1
0026  8      IF(NFIN-NST+1.EQ.NINTRP)GO TO 7
0028      IF(XX-X(NST).GT.X(NFIN)-XX)GO TO 6
0030      NST=NST-1
0031      IF(NST.EQ.1)GO TO 5
0033      GO TO 8
0034  6      NFIN=NFIN+1
0035      IF(NFIN.EQ.NPTS)GO TO 10
0037      GO TO 8
0038  7      SEX=0.D0
0039      DO 1 I=NST,NFIN
0040      TOP=1.D0
0041      BOT=1.D0
0042      DO 2 J=NST,NFIN
0043      IF(I.EQ.J) GO TO 2
0045      TOP=TOP*(XX-X(J))
0046      BOT=BOT*(X(I)-X(J))
0047  2      CONTINUE
0048  1      SEX=SEX+Y(I)*TOP/BOT
0049      IF(ISWICH(8).EQ.1)WRITE(5,165)(X(I),Y(I),I=NST,NFIN)
0051  165    FORMAT(1X,2D14.6)
0052      IF(ISWICH(2).EQ.1)WRITE(5,165)XX,SEX
0054      RETURN
0055      END

```

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:09:03

PAGE 001

```

0001      SUBROUTINE STATE(X,R,PE,GE)
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      COMMON/ DATA1/ SI,W
0004      DIMENSION D(2),E(4),A(4)
0005      A(1)=X
0006      DO 26 I=1,3
0007 26      A(I+1)=W*A(I)
0008      A(1)=1. DO
0009      DO 27 I=2,4
0010 27      A(I)=1. DO-X+A(I)
0011      B0=A(3)*(A(3)/A(4))**Z
0012      B1=A(2)*A(3)/A(4)
0013      B2=R/A(4)
0014      D2=1. DO-R
0015      D1=1. DO/(1. DO-R)
0016      A1=-(1. DO-B0)*DLOG(D2)+(B0*D1+3. DO*B1)*R*D1
0017      Z0=D1*(1. DO+(3. DO*A(2)+(3. DO-R)*B2*A(3)**Z*D1)*B2*A(3)*D1)
0018      SE=-A1
0019      GE=Z0-1. DO-SE
0020      PE=Z0*B2
0021      RETURN
0022      END

```

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:08:04

PAGE 001

```

0001      SUBROUTINE BASIS(J,Q1,Q2,Q3)
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      COMMON /DATA1/ SI,W,XM,RW,DW
0004      COMMON /DATA2/ F(5),D(2),X
0005      Z1=J*D(1)
0006      Z2=J*D(2)
0007      Z5=1. DO-X
0008      Z3=Z5*Z1*W
0009      Z4=Z5*Z2*RW
0010      X7=Z1*Z2*X
0011      X8=1. DO/(1. DO-Z1-Z2+X7)
0012      A1=(4. DO*(1. DO-Z2*X)+3. DO*(Z1+Z4-X7*(2. DO-Z2*X))*X8)*X8
0013      A2=((3. DO+W)+3. DO*X8*(Z1*W+Z2-(1. DO+W)*X7))*X8
0014      A3=((3. DO+1. DO/W)+3. DO*X8*(Z2/W+Z1-(1. DO+1. DO/W)*X7))*X8
0015      A4=(4. DO*(1. DO-Z1*X)+3. DO*X8*(Z3+Z2-X7*(2. DO-Z1*X))*X8
0016      Q1=2. DO*A1+Z1*A1*A1+Z4*A3*A3
0017      Q2=2. DO*A4+Z2*A4*A4+Z3*A2*A2
0018      Q3=(W*A3+W*W*A2+W*W*A1*A2*Z1+W*Z2*A3*A4)*DW
0019      RETURN
0020      END

```

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:11:06

PAGE 001

```

0001      SUBROUTINE POLYFT(X0,X1,X2,XP)
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      DIMENSION X(4),G(4)
0004      COMMON/DATA10/F(4)
0005      X(1)=X0
0006      X(2)=X1
0007      X(3)=X2
0008      SUM=0. D0
0009      DO 10 I=1,3
0010      G(I)=F(I)
0011      DO 11 J=1,3
0012      IF (J.EQ. I) GO TO 11
0014      G(I)=G(I)/(X(I)-X(J))
0015 11      CONTINUE
0016      SUM=SUM+G(I)
0017 10      CONTINUE
0018      F0=G(1)/SUM
0019      F1=G(2)/SUM
0020      F2=G(3)/SUM
0021      C=X2*X1*F0+X2*X0*F1+X1*X0*F2
0022      B=.5D0*((X1+X2)*F0+(X0+X2)*F1+(X0+X1)*F2)
0023      FF=F(4)/SUM
0024      CF=B*B-C+FF
0025      IF (CF.LT. 0) GO TO 20
0027      DCF=DSQRT(CF)
0028      XP=B+DCF
0029      XM=B-DCF
0030      GO TO 300
0031 20      WRITE(5,100)
0032 100      FORMAT(' IMAGINARY ROOTS')
0033      STOP
0034 300      RETURN
0035      END

```

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:08:18

PAGE 001

```

0001      SUBROUTINE WORK
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      COMMON /DATA2/ F(5),D(2),X
0004      COMMON /DATA1/S1,W
0005      CALL BASIS(2,S8,S7,S6)
0006      CALL BASIS(-1,Q1,Q2,Q3)
0007      F(1)=Q1+2. D0*S8
0008      F(2)=Q2+2. D0*S7
0009      F(3)=Q3+2. D0*S6
0010      F(4)=1. D0-(1. D0-X)*F(3)*F(3)/(F(1)*F(2))
0011      F(5)=D(2)-S1*F(1)*D(1)/F(2)
0012      RETURN
0013      END

```

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:11:24

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```

0001      FUNCTION SUM(AA, BB, M, N, J)
0002      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
0003      DIMENSION A(16), W(16)
0004      COMMON /DATA3/ Y(200), X(200)
0005      CALL GAUSS(M, A, W)
0006      SUM=0. D0
0007      MZ=M/Z
0008      IF (ISWICH(8). EQ. 1) WRITE(5, 155) (A(J), W(J), J=1, MZ)
0010 155    FORMAT(1X, 2D14:6)
0011      DO 1 I=1, M2
0012      XP=((BB-AA)*A(I)+(BB+AA))/2. D0
0013      XM=((AA-EB)*A(I)+(BB+AA))/2. D0
0014      SUM=SUM+W(I)*(SEX(J, N, X, Y, XP)+SEX(J, N, X, Y, XM))
0015 1      IF (ISWICH(7). EQ. 1) WRITE(5, 156) XP, XM, SUM
0017 156    FORMAT(1X, 3D14:6)
0018      SUM=SUM/2. D0
0019      RETURN
0020      END

```

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:09:16

PAGE 001

```

0001      FUNCTION CHANGE(RHO, FMIXT)
0002      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
0003      COMMON/DATA1/S1, W
0004      COMMON/DATA5/S0, BB, FM
0005      COMMON/DATA7/E3, E2
0006      DELTA=1. D-06
0007      R1=RHO*(1. D0+DELTA)
0008      R2=RHO*(1. D0-DELTA)
0009      E3=(FMIX(R1)-FMIX(R2))/(2. D0*DELTA*RHO)
0010      E4=FMIX(RHO)
0011      E2=FMIXT-E4
0012      CHANGE=E2/(E3)
0013      RETURN
0014      END

```

RT-11 FORTRAN IV

VO1B-08 MON 16-MAY-77 15:12:16

PAGE 001

```

0001      SUBROUTINE GAUSS(M,A,W)
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      DIMENSION A(16),W(16)
0004      IF(M.NE.4) GO TO 1
0006      A(1)=.33998104
0007      A(2)=.86113631
0008      W(1)=.65214515
0009      W(2)=.34785484
0010      RETURN
0011  1      IF(M.NE.8) GO TO 2
0013      A(1)=.18343464
0014      A(2)=.52553240
0015      A(3)=.79666647
0016      A(4)=.96028985
0017      W(1)=.36268378
0018      W(2)=.31370664
0019      W(3)=.22238103
0020      W(4)=.10122853
0021      RETURN
0022  2      IF(M.NE.16) GO TO 3
0024      A(1)=.09501250
0025      A(2)=.28160355
0026      A(3)=.45801677
0027      A(4)=.61787624
0028      A(5)=.75540440
0029      A(6)=.86563120
0030      A(7)=.94457502
0031      A(8)=.98940093
0032      W(1)=.18945061
0033      W(2)=.18260341
0034      W(3)=.16915651
0035      W(4)=.14959598
0036      W(5)=.12462897
0037      W(6)=.09515851
0038      W(7)=.06225352
0039      W(8)=.02715245
0040      RETURN
0041  3      IF(M.NE.32) STOP
0043      A(1)=.04830766
0044      A(2)=.14447196
0045      A(3)=.23928736
0046      A(4)=.33186860
0047      A(5)=.42135127
0048      A(6)=.50689990
0049      A(7)=.58771575
0050      A(8)=.66304426
0051      A(9)=.73218211
0052      A(10)=.79448379
0053      A(11)=.84936761
0054      A(12)=.89632115
0055      A(13)=.93490607
0056      A(14)=.96476225
0057      A(15)=.98561151
0058      A(16)=.99726386
0059      W(1)=.09654008
0060      W(2)=.09563872
0061      W(3)=.09384439

```

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:12:16

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0062	W(4)=.09117387
0063	W(5)=.08765209
0064	W(6)=.08331192
0065	W(7)=.07819389
0066	W(8)=.07234579
0067	W(9)=.06582222
0068	W(10)=.05868409
0069	W(11)=.05099805
0070	W(12)=.04283589
0071	W(13)=.03427386
0072	W(14)=.02539206
0073	W(15)=.01627439
0074	W(16)=.00701861
0075	RETURN
0076	END

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:07:48

PAGE 001

```

0001      FUNCTION NEWTON(X,B,P)
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      REAL*8 NEWTON
0004      COMMON/DATA4/P2,P5,Y,IFLAG,DNEW
0005      COMMON/DATA5/S0,BB,FM
0006      IFLAG=0
0007      I      Y1=1. D0+4. D0*X
0008      Y2=1. D0-2. D0*X
0009      Y3=1. D0*X
0010      Y=((Y1/Y2**2)**2-(Y2/Y3**2)**2)/B
0011      IF(Y.LT. 1. D0)GO TO 10
0013      X=. 98D0*X
0014      IFLAG=IFLAG+1
0015      GO TO 1
0016      10      D6=(16. D0*Y1*Y3/Y2**5+4. D0*Y2*(2. D0-X)/Y3**5)/B**2
0017      DNEW=X
0018      P0=Y*(1. D0+Y*(1. D0+Y*(1. D0-Y)))/(1. D0-Y)**3/B
0019      P1=X*X*(8. D0*(Y3/Y2**2)**2+((2. D0-X)/Y3**2)**2)/B
0020      IF(FM.EQ. 1. D0)AMP=S0*S0
0022      IF(FM.EQ. 0. D0)AMP=1. D0
0024      P2=(P0-Y*X+P1)=P/AMP
0025      P4=P0-Y*X+P1
0026      100      FORMAT(1X,4F16.8)
0027      P3=((1. D0+4. D0*Y*(1. D0+Y*(1. D0-Y*(1. D0-. 25D0*Y))))/(1. D0-Y)**
0028      P3=P3*D6-Y
0029      P5=P3/D6
0029      C      IF(ISWICH(10).EQ. 1)WRITE(5,100)X,Y,P5,P2
0030      NEWTON=P2/P3
0031      RETURN
0032      END

```

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:11:35

PAGE 001

```

0001      FUNCTION GIBBS(B,P,RHO)
0002      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0003      COMMON/DATA4/ P2,P3,Y,IFLAG,DNEW
0004      COMMON/DATA1/S1,W,XM
0005      COMMON/DATA5/S0,BB,FM
0006      COMMON/DATA8/Y0,Y10
0007      REAL*8 NEWTON
0008      DELTA=5. D-02
0009      TOL=1. D-09
0010      T1=SECNDS(0.)
0011      IF(FM.EQ.1.0D0)D=RHO
0013      IF(FM.EQ.0.0D0)D=D/S0
0015      I=1
0016      2   J=1
0017      1   M=1
0018      5   D2=-NEWTON(D,B,P)/2. DO**(M-1)
0019      IF(IFLAG.NE.0)D=DNEW
0021      IF(J.GT.201)GO TO 43
0023      IF(DABS(D2/D).LT.DELTA)GO TO 15
0025      M=M+1
0026      GO TO 5
0027      43  D2=1. D-02
0028      D=.4D0
0029      45  ISPY=0
0030      Y1=NEWTON(D,B,P)
0031      P3=P2
0032      IF(IFLAG.NE.0)D=DNEW
0034      DO 50 K=1,3,2
0035      DCH=D*(K-2)*D2
0036      Y1=NEWTON(DCH,B,P)
0037      IF(IFLAG.NE.0)D=DNEW
0039      P1=P2
0040      IF(DABS(P1).GT.DABS(P3))GO TO 50
0042      ISPY=1
0043      P3=P1
0044      D1=DCH
0045      50  CONTINUE
0046      IF(ISPY.GT.0)GO TO 55
0048      D2=D2/2. D0
0049      GO TO 45
0050      55  D=D1
0051      IF(ISWICH(10).EQ.1)WRITE(5,191)D,Y,D2,P3
0053      191  FORMAT(3F14.6,D16.7)
0054      T2=SECNDS(T1)
0055      IF(T2.GT.600)GO TO 85
0057      IF(DABS(P2).LT.TOL)GO TO 25
0059      IF(DABS(D2).GT.TOL)GO TO 45
0061      WRITE(5,120)
0062      120  FORMAT(1X,'NO LIQUID SOLUTION FOUND')
0063      T1=SECNDS(0.)
0064      D=1. D-03
0065      D2=5. D-04
0066      ISERR=1
0067      GO TO 45
0068      15  D=D+D2
0069      IF(M.EQ.1)Y3=NEWTON(D,B,P)
0071      IF(IFLAG.NE.0)D=DNEW

```

RT-11 FORTRAN IV

V01B-08

MON 16-MAY-77 15:11:35

PAGE 002

```

0073 20  IF(ISWICH(10).EQ.1)WRITE(5,100)D,Y,P2,P5,J,M
0075 100  FORMAT(4F14.6,2I4)
0076      J=J+1
0077      IF(DABS(P2).LT.1.D-09)GO TO 25
0079      IF(J.LT.301)GO TO 1
0081      D=.3D0-I*.005
0082      I=I+1
0083      IF(I.LT.10)GO TO 2
0085 85  WRITE(5,110)B,P,P2
0086 110  FORMAT(1X,'BETA=',F6.3,'AND PRESSURE =',F9.6,'TOL=',D14.6)
0087      RETURN
0088 25  P9=Y
0089      E1=B*D
0090      D9=1.D0/(1.D0-P9)
0091      A9=(D9+3.D0)*D9*P9
0092      Z9=D9+(3.D0+(3.D0-P9)*P9*D9)*P9*D9**2
0093      S9=-A9
0094      G9=Z9-1.D0-S9
0095      B1=8.D0*BB*S0*XM
0096      ZPURE=P*B/Y
0097      IF(B.EQ.B1)ZPURE=ZPURE/(S0*S0)
0099      IF(B.EQ.B1)Y10=Y
0101      B0=8.D0*BB
0102      IF(B.EQ.B0)Y0=Y
0104      GIBBS=-E1+G9-DLOG(ZPURE)
0105      GHSD=-E1+G9
0106      ZDPURE=DLOG(ZPURE)
0107      IF(ISWICH(14).EQ.1)WRITE(5,150)GIBBS,GHSD,ZDPURE,Y
0109 150  FORMAT(1X,3F14.6,2D16.8)
0110      RETURN
0111      END

```

RT-11 FORTRAN IV

V01B-08

MON 24-MAY-76 17:48:19

```

0001      DIMENSION CP(50),GMIX(50),GPURE(50),GXS(50),FX(50)
          1,TOL(50),DEN(50)
0002      DIMENSION GINT(101),X(25)
0003      1      TYPE 500
0004      500    FORMAT('ENTER DATA FILE ')
0005      CALL ASSIGN(1,-1)
0006      251    FORMAT(1X,F5.2,3F14.6,E16.7)
0007      DO 2 I=1,25
0008      READ(1,251)FX(I),DEN(I),GMIX(I),GXS(I),TOL(I)
0009      2      TYPE 251,FX(I),DEN(I),GMIX(I),GXS(I),TOL(I)
0010      2      CONTINUE
0011      XM=(GMIX(25)-GMIX(1))/24
0012      DO 3 I=1,25
0013      GMIX(I)=GMIX(I)-XM*FLOAT(I-1)
0014      30      DO 30 I=1,25
0015      X(I)=I
0016      DO 40 J=1,97
0017      XX=(J-1)*.25+1
0018      GINT(J)=SEX(4,25,X,GMIX,XX)
0019      CALL OKPLT(97,GINT)
0020      33      TYPE 33
0021      33      FORMAT('INPUT NUMBER PTS APART ')
0022      ACCEPT 34,L
0023      IF(L.EQ.0)CALL EXIT
0024      34      FORMAT(I4)
0025      CALL COMTAN(GINT,97,I1,I2,L)
0026      WRITE(5,120)I1,I2,L
0027      GO TO 28
0028      120     FORMAT(1X,3I6)
0029      CALL EXIT
0030      END

```

RT-11 FORTRAN IV

V01B-08

MON 24-MAY-76 17:48:50

```

0001      SUBROUTINE COMTAN(A,N,I1,I2,L)
0002      DIMENSION A(1),AD(100)
0003      M=N-2
0004      I1=0
0005      I2=0
0006      MM=M-1
0007      DO 1 I=3,M
0008      1      AD(I)=(A(I-2)-A(I+2))/12.+2*(A(I+1)-A(I-1))/3.
0009      MM=M-L
0010      XMAX=1.E06
0011      DO 2 I=3,MM
0012      II=I+L
0013      DO 2 J=II,M
0014      XM=(A(J)-A(I))/(J-I)
0015      X=AMAX1(ABS(XM-AD(I)),ABS(XM-AD(J)))
0016      IF(X.GT.XMAX)GO TO 2
0017      XMAX=X
0018      II=I
0019      I2=J
0020      2      CONTINUE
0021      RETURN
0022      END

```

Appendix 10(X, RHO, GMIXT, GXS, TOL) Data

The following pages are a representative sample of the data obtained from the batch jobs. The five columns are mole fraction, volume density required at that mole fraction to ensure the pressure is constant at the initiated value, GMIXT, GXS, and the difference between the initial and convergent pressure values. The first row of (X, RHO, GMIXT, GXS) values are the  $x = 0$  results given from Adelman and Deutch's (1973) equations.

29-JAN-77  
 32POINTS AT INTERVALS OF 0.184  
 DENSITY= 0.365RATIO OF DIPOLES= 1.50RATIO OF RADII=1.010  
 8POINT QUAD 6POINTS FOR INTERP GIVEN 32  
 TEMP= 0.1700 ET PRESSURE= 0.001383

X	DENSITY	GMIXTURE	GMIXING
0.00	0.220765	-2.965384	0.000000
TIME TAKEN WAS 12.97MINS			
0.00	0.220765	-2.965385	-0.000001
0.04	0.230840	-3.477738	-0.079932
0.08	0.240278	-3.944134	-0.113907
0.12	0.249145	-4.398216	-0.135568
0.16	0.257500	-4.846466	-0.151396
0.20	0.265394	-5.291652	-0.164161
0.24	0.272872	-5.735161	-0.175249
0.28	0.279972	-6.177736	-0.185402
0.32	0.286728	-6.619768	-0.195013
0.36	0.293169	-7.061438	-0.204261
0.40	0.299321	-7.502785	-0.213186
0.44	0.305208	-7.943752	-0.221733
0.48	0.310850	-8.384208	-0.229767
0.52	0.316265	-8.823952	-0.237090
0.56	0.321470	-9.262727	-0.243444
0.60	0.326478	-9.700210	-0.248504
0.64	0.331304	-10.136004	-0.251878
0.68	0.335960	-10.569626	-0.253078
0.72	0.340455	-11.000472	-0.251502
0.76	0.344800	-11.427774	-0.246383
0.80	0.349005	-11.850520	-0.236708
0.84	0.353077	-12.267302	-0.221069
0.88	0.357023	-12.676017	-0.197362
0.92	0.360852	-13.073131	-0.162054
0.96	0.364566	-13.451314	-0.107816
1.00	0.368174	-13.775919	0.000000

29-JAN-77  
 32POINTS AT INTERVALS OF 0.174  
 DENSITY= 0.355RATIO OF DIPOLES= 1.50RATIO OF RADII=1.010  
 8POINT QUAD 6POINTS FOR INTERP GIVEN 32  
 TEMP= 0.1800 ET PRESSURE= 0.001383

X	DENSITY	GMIXTURE	GMIXING
0.00	0.206617	-2.542123	0.000000
TIME TAKEN WAS 13.08MINS			
0.00	0.206617	-2.542124	-0.000001
0.04	0.217099	-3.020470	-0.081283
0.08	0.226901	-3.452820	-0.116569
0.12	0.236097	-3.872789	-0.139474
0.16	0.244749	-4.286835	-0.156456
0.20	0.252912	-4.697712	-0.170269
0.24	0.260635	-5.106794	-0.182288
0.28	0.267958	-5.514817	-0.193246
0.32	0.274920	-5.922166	-0.203532
0.36	0.281550	-6.329019	-0.213320
0.40	0.287878	-6.735413	-0.222651
0.44	0.293928	-7.141293	-0.231466
0.48	0.299722	-7.546524	-0.239633
0.52	0.305279	-7.950909	-0.246954
0.56	0.310617	-8.354190	-0.253172
0.60	0.315751	-8.756047	-0.257965
0.64	0.320696	-9.156086	-0.260940
0.68	0.325463	-9.553825	-0.261615
0.72	0.330064	-9.948662	-0.259388
0.76	0.334510	-10.339833	-0.253495
0.80	0.338810	-10.726326	-0.242925
0.84	0.342973	-11.106738	-0.226273
0.88	0.347007	-11.478968	-0.201438
0.92	0.350918	-11.839484	-0.164891
0.96	0.354712	-12.180964	-0.109307
1.00	0.358397	-12.468721	0.000000

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32POINTS AT INTERVALS OF 0.164

DENSITY= 0.345 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1900 ET PRESSURE= 0.001383

X	DENSITY	GMIXTURE	GMIXING
0.00	0.192587	-2.178480	0.000000
TIME TAKEN WAS	13.27MINS		
0.00	0.192587	-2.178480	-0.000000 0.2392834E-15
0.04	0.203506	-2.626323	-0.082219 0.5443183E-13
0.08	0.213702	-3.028203	-0.118474 0.3069908E-13
0.12	0.223251	-3.417688	-0.142334 0.1108426E-10
0.16	0.232221	-3.801213	-0.160235 0.6000553E-11
0.20	0.240670	-4.181509	-0.174906 0.3383123E-11
0.24	0.248653	-4.559932	-0.187704 0.1979016E-11
0.28	0.256213	-4.937205	-0.199353 0.1196754E-11
0.32	0.263390	-5.313706	-0.210229 0.7456866E-12
0.36	0.270219	-5.689606	-0.220505 0.4773331E-12
0.40	0.276730	-6.064940	-0.230213 0.3130535E-12
0.44	0.282949	-6.439646	-0.239295 0.2098899E-12
0.48	0.288900	-6.813591	-0.247616 0.1435433E-12
0.52	0.294604	-7.186578	-0.254977 0.9997656E-13
0.56	0.300079	-7.558347	-0.261122 0.7078637E-13
0.60	0.305341	-7.928578	-0.265729 0.5088909E-13
0.64	0.310406	-8.296881	-0.268406 0.3709153E-13
0.68	0.315287	-8.662771	-0.268673 0.2737882E-13
0.72	0.319997	-9.025652	-0.265929 0.2046161E-13
0.76	0.324545	-9.384759	-0.259411 0.1544218E-13
0.80	0.328942	-9.739083	-0.248110 0.1178799E-13
0.84	0.333197	-10.087222	-0.230625 0.9090493E-14
0.88	0.337318	-10.427077	-0.204855 0.7040917E-14
0.92	0.341313	-10.755121	-0.167274 0.5530841E-14
0.96	0.345187	-11.064030	-0.110558 0.4333014E-14
1.00	0.348949	-11.319096	0.000000

29-JAN-77

32POINTS AT INTERVALS OF 0.156

DENSITY= 0.336 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.2000 ET PRESSURE= 0.001383

X	DENSITY	GMIXTURE	GMIXING
0.00	0.178597	-1.865063	0.000000
TIME TAKEN WAS	13.45MINS		
0.00	0.178597	-1.865063	-0.000000 0.2005774E-16
0.04	0.189988	-2.285277	-0.082744 0.8936526E-13
0.08	0.200611	-2.659633	-0.119630 0.4975892E-13
0.12	0.210543	-3.021643	-0.144169 0.2812930E-13
0.16	0.219855	-3.377711	-0.162767 0.1008802E-10
0.20	0.228613	-3.730532	-0.178117 0.5491920E-11
0.24	0.236872	-4.081442	-0.191558 0.3111802E-11
0.28	0.244684	-4.431148	-0.203793 0.1828747E-11
0.32	0.252089	-4.780014	-0.215188 0.1110646E-11
0.36	0.259127	-5.128201	-0.225906 0.6948258E-12
0.40	0.265830	-5.475738	-0.235973 0.4464234E-12
0.44	0.272226	-5.822561	-0.245325 0.2938085E-12
0.48	0.278340	-6.168530	-0.253824 0.1976198E-12
0.52	0.284196	-6.513447	-0.261270 0.1355696E-12
0.56	0.289812	-6.857051	-0.267405 0.9467177E-13
0.60	0.295208	-7.199023	-0.271906 0.6720893E-13
0.64	0.300397	-7.538970	-0.274383 0.4842405E-13
0.68	0.305395	-7.876410	-0.274353 0.3537806E-13
0.72	0.310214	-8.210746	-0.271219 0.2617405E-13
0.76	0.314866	-8.541215	-0.264217 0.1959251E-13
0.80	0.319361	-8.866809	-0.252341 0.1483416E-13
0.84	0.323710	-9.186127	-0.234189 0.1133436E-13
0.88	0.327920	-9.497072	-0.207663 0.8756559E-14
0.92	0.332000	-9.796118	-0.169239 0.6809332E-14
0.96	0.335954	-10.075939	-0.111590 0.5338286E-14
1.00	0.339795	-10.301819	0.000000

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32POINTS AT INTERVALS OF 0.164

DENSITY= 0.347RATIO OF DIPOLES= 1.50RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1900 ET PRESSURE= 0.001844

X	DENSITY	GMIXTURE	GMIXING
0.00	0.201605	-2.367717	0.000000
TIME TAKEN WAS 13.08MINS			
0.00	0.201605	-2.367717	-0.000000 0.4125931E-15
0.04	0.211551	-2.820387	-0.085393 0.2121366E-13
0.08	0.220938	-3.226370	-0.124100 0.7937112E-11
0.12	0.229810	-3.619387	-0.149840 0.4724204E-11
0.16	0.238205	-4.005983	-0.169161 0.2790404E-11
0.20	0.246165	-4.388975	-0.184876 0.1710746E-11
0.24	0.253724	-4.769784	-0.198409 0.1073360E-11
0.28	0.260916	-5.149185	-0.210534 0.6885796E-12
0.32	0.267771	-5.527597	-0.221669 0.4511627E-12
0.36	0.274316	-5.905222	-0.232018 0.3015133E-12
0.40	0.280575	-6.282122	-0.241641 0.2052466E-12
0.44	0.286569	-6.658257	-0.250500 0.1421347E-12
0.48	0.292318	-7.033512	-0.258478 0.1000174E-12
0.52	0.297839	-7.407702	-0.265392 0.7141960E-13
0.56	0.303149	-7.780583	-0.270996 0.5169275E-13
0.60	0.308261	-8.151844	-0.274981 0.3790430E-13
0.64	0.313189	-8.521103	-0.276964 0.2813478E-13
0.68	0.317945	-8.887885	-0.276469 0.2109180E-13
0.72	0.322538	-9.251598	-0.272906 0.1597523E-13
0.76	0.326980	-9.611484	-0.265516 0.1224384E-13
0.80	0.331278	-9.966540	-0.253295 0.9441395E-14
0.84	0.335442	-10.315366	-0.234846 0.7356258E-14
0.88	0.339478	-10.655869	-0.208072 0.5778527E-14
0.92	0.343394	-10.984524	-0.169451 0.4554679E-14
0.96	0.347194	-11.294011	-0.111661 0.3626602E-14
1.00	0.350888	-11.549626	0.000000

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32POINTS AT INTERVALS OF 0.156

DENSITY= 0.338RATIO OF DIPOLES= 1.50RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.2000 ET PRESSURE= 0.001844

X	DENSITY	GMIXTURE	GMIXING
0.00	0.188656	-2.052377	0.000000
TIME TAKEN WAS 13.23MINS			
0.00	0.188656	-2.052378	-0.000000 0.6044427E-16
0.04	0.198895	-2.478046	-0.086413 0.3049443E-13
0.08	0.208568	-2.856991	-0.126103 0.1919705E-13
0.12	0.217710	-3.222913	-0.152771 0.7132775E-11
0.16	0.226360	-3.582356	-0.172958 0.4205058E-11
0.20	0.234555	-3.938117	-0.189464 0.2533983E-11
0.24	0.242333	-4.291613	-0.203705 0.1561773E-11
0.28	0.249729	-4.643610	-0.216447 0.9848005E-12
0.32	0.256773	-4.994523	-0.228105 0.6347758E-12
0.36	0.263494	-5.344550	-0.238877 0.4177294E-12
0.40	0.269916	-5.693751	-0.248823 0.2803059E-12
0.44	0.276063	-6.042085	-0.257902 0.1915501E-12
0.48	0.281955	-6.389435	-0.265996 0.1331259E-12
0.52	0.287611	-6.735617	-0.272924 0.9397707E-13
0.56	0.293047	-7.080387	-0.278438 0.6731697E-13
0.60	0.298278	-7.423436	-0.282232 0.4886949E-13
0.64	0.303318	-7.764380	-0.283921 0.3592585E-13
0.68	0.308180	-8.102748	-0.283034 0.2672271E-13
0.72	0.312874	-8.437949	-0.278980 0.2009086E-13
0.76	0.317412	-8.769226	-0.271001 0.1526226E-13
0.80	0.321801	-9.095576	-0.258097 0.1170955E-13
0.84	0.326052	-9.415605	-0.238871 0.9059756E-14
0.88	0.330171	-9.727219	-0.211229 0.7068293E-14
0.92	0.334166	-10.026895	-0.171650 0.5540869E-14
0.96	0.338042	-10.307311	-0.112811 0.4389880E-14
1.00	0.341809	-10.533755	0.000000

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 32POINTS AT INTERVALS OF 0.149  
 DENSITY= 0.329 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.010  
 8POINT QUAD 6POINTS FOR INTERP GIVEN 32  
 TEMP= 0.2100 ET PRESSURE= 0.001844

X	DENSITY	GMIXTURE	GMIXING
0.00	0.175873	-1.779058	0.000000
TIME TAKEN WAS 13.47MINS			
0.00	0.175873	-1.779058	-0.000000 0.8131516E-18
0.04	0.186399	-2.180229	-0.087139 0.4338907E-13
0.08	0.196362	-2.534678	-0.127556 0.2772625E-13
0.12	0.205783	-2.876088	-0.154934 0.1748206E-13
0.16	0.214695	-3.210991	-0.175804 0.6445652E-11
0.20	0.223137	-3.542170	-0.192952 0.3818990E-11
0.24	0.231144	-3.871031	-0.207781 0.2312007E-11
0.28	0.238752	-4.198331	-0.221049 0.1431898E-11
0.32	0.245993	-4.524476	-0.233161 0.9070268E-12
0.36	0.252896	-4.849659	-0.244312 0.5871377E-12
0.40	0.259488	-5.173935	-0.254557 0.3879364E-12
0.44	0.265794	-5.497262	-0.263852 0.2613063E-12
0.48	0.271833	-5.819519	-0.272077 0.1791936E-12
0.52	0.277628	-6.140523	-0.279049 0.1249393E-12
0.56	0.283193	-6.460027	-0.284521 0.8847063E-13
0.60	0.288547	-6.777723	-0.288185 0.6355956E-13
0.64	0.293702	-7.093227	-0.289657 0.4625960E-13
0.68	0.298673	-7.406069	-0.288467 0.3409875E-13
0.72	0.303470	-7.715657	-0.284023 0.2542600E-13
0.76	0.308104	-8.021237	-0.275571 0.1915498E-13
0.80	0.312586	-8.321807	-0.262109 0.1459613E-13
0.84	0.316925	-8.615973	-0.242243 0.1120301E-13
0.88	0.321128	-8.901643	-0.213881 0.8680719E-14
0.92	0.325203	-9.175295	-0.173501 0.6777727E-14
0.96	0.329156	-9.429603	-0.113778 0.5313621E-14
1.00	0.332996	-9.629858	0.000000

30-JAN-77  
 32POINTS AT INTERVALS OF 0.142  
 DENSITY= 0.321 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.010  
 8POINT QUAD 6POINTS FOR INTERP GIVEN 32  
 TEMP= 0.2200 ET PRESSURE= 0.001844

X	DENSITY	GMIXTURE	GMIXING
0.00	0.163237	-1.541739	0.000000
TIME TAKEN WAS 13.65MINS			
0.00	0.163237	-1.541739	0.000000 0.5800482E-17
0.04	0.174032	-1.920521	-0.087588 0.6025123E-13
0.08	0.184280	-2.252615	-0.128488 0.3974897E-13
0.12	0.193986	-2.571689	-0.156368 0.2536659E-13
0.16	0.203172	-2.884263	-0.177748 0.1597957E-13
0.20	0.211870	-3.193105	-0.195396 0.5859244E-11
0.24	0.220117	-3.499603	-0.210700 0.3485668E-11
0.28	0.227947	-3.804504	-0.224407 0.2119292E-11
0.32	0.235394	-4.108203	-0.236912 0.1318148E-11
0.36	0.242488	-4.410887	-0.248402 0.8383968E-12
0.40	0.249257	-4.712605	-0.258926 0.5448378E-12
0.44	0.255727	-5.013308	-0.268435 0.3613288E-12
0.48	0.261921	-5.312873	-0.276807 0.2442184E-12
0.52	0.267858	-5.611115	-0.283854 0.1680107E-12
0.56	0.273558	-5.907784	-0.289330 0.1175125E-12
0.60	0.279037	-6.202571	-0.292923 0.8344383E-13
0.64	0.284311	-6.495094	-0.294252 0.6009619E-13
0.68	0.289392	-6.784879	-0.292843 0.4385354E-13
0.72	0.294295	-7.071337	-0.288107 0.3240089E-13
0.76	0.299029	-7.353713	-0.279288 0.2421430E-13
0.80	0.303605	-7.631005	-0.265387 0.1829542E-13
0.84	0.308033	-7.901821	-0.245009 0.1394387E-13
0.88	0.312322	-8.164070	-0.216064 0.1073376E-13
0.92	0.316478	-8.414230	-0.175030 0.8343315E-14
0.96	0.320508	-8.644970	-0.114576 0.6548744E-14
1.00	0.324423	-8.821588	0.000000

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32POINTS AT INTERVALS OF 0.136

DENSITY= 0.312 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.2300 ET PRESSURE= 0.001844

X	DENSITY	GMIXTURE	GMIXING
0.00	0.150753	-1.335545	0.000000
TIME TAKEN WAS 13.85MINS			
0.00	0.150753	-1.335545	0.000000 0.1338990E-16
0.04	0.161773	-1.693728	-0.087782 0.7987832E-13
0.08	0.172294	-2.005279	-0.128931 0.5583072E-13
0.12	0.182285	-2.303860	-0.157111 0.3491993E-13
0.16	0.191751	-2.595981	-0.178831 0.2331636E-13
0.20	0.200717	-2.884392	-0.196841 0.1470498E-13
0.24	0.209215	-3.170464	-0.212512 0.5353724E-11
0.28	0.217278	-3.454928	-0.226575 0.3196345E-11
0.32	0.224942	-3.738169	-0.239415 0.1950878E-11
0.36	0.232236	-4.020362	-0.251207 0.1218026E-11
0.40	0.239191	-4.301548	-0.261992 0.7776134E-12
0.44	0.245833	-4.581673	-0.271716 0.5071305E-12
0.48	0.252186	-4.860609	-0.280250 0.3374607E-12
0.52	0.258273	-5.138164	-0.287405 0.2288249E-12
0.56	0.264112	-5.414090	-0.292929 0.1578964E-12
0.60	0.269721	-5.688073	-0.296511 0.1107371E-12
0.64	0.275117	-5.959728	-0.297766 0.7884421E-13
0.68	0.280313	-6.228584	-0.296221 0.5693249E-13
0.72	0.285324	-6.494049	-0.291284 0.4164177E-13
0.76	0.290160	-6.755368	-0.282202 0.3082707E-13
0.80	0.294833	-7.011541	-0.267974 0.2308326E-13
0.84	0.299352	-7.261173	-0.247205 0.1746623E-13
0.88	0.303727	-7.502175	-0.217806 0.1334713E-13
0.92	0.307966	-7.731027	-0.176256 0.1029141E-13
0.96	0.312076	-7.940383	-0.115212 0.7961676E-14
1.00	0.316066	-8.095572	0.000000

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32POINTS AT INTERVALS OF 0.184

DENSITY= 0.373 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.000

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1700 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.237919	-3.335199	0.000000
TIME TAKEN WAS 9.62MINS			
0.00	0.237919	-3.335201	-0.000002 0.6459622E-14
0.04	0.246857	-3.872399	-0.074184 0.3014317E-11
0.08	0.255349	-4.363842	-0.102612 0.1956991E-11
0.12	0.263423	-4.843260	-0.119014 0.1280940E-11
0.16	0.271105	-5.317263	-0.130002 0.8478478E-12
0.20	0.278425	-5.788664	-0.138387 0.5684263E-12
0.24	0.285408	-6.258889	-0.145596 0.3862687E-12
0.28	0.292078	-6.728709	-0.152401 0.2661126E-12
0.32	0.298458	-7.198533	-0.159209 0.1858083E-12
0.36	0.304567	-7.668551	-0.166211 0.1314460E-12
0.40	0.310426	-8.138810	-0.173455 0.9416984E-13
0.44	0.316050	-8.609254	-0.180883 0.6828213E-13
0.48	0.321456	-9.079748	-0.188361 0.5006276E-13
0.52	0.326657	-9.550091	-0.195689 0.3712043E-13
0.56	0.331668	-10.020019	-0.202601 0.2778935E-13
0.60	0.336500	-10.489203	-0.208770 0.2101786E-13
0.64	0.341163	-10.957242	-0.213793 0.1604007E-13
0.68	0.345669	-11.423643	-0.217178 0.1235551E-13
0.72	0.350026	-11.887796	-0.218316 0.9576487E-14
0.76	0.354243	-12.348925	-0.216430 0.7489614E-14
0.80	0.358327	-12.806011	-0.210500 0.5909281E-14
0.84	0.362286	-13.257638	-0.199111 0.4680230E-14
0.88	0.366127	-13.701694	-0.180152 0.3742612E-14
0.92	0.369856	-14.134640	-0.150082 0.3014028E-14
0.96	0.373477	-14.549127	-0.101554 0.2416416E-14
1.00	0.376995	-14.910589	0.000000

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32POINTS AT INTERVALS OF 0.208

DENSITY= 0.390RATIO OF DIPOLES= 1.50RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1500 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.264276	-4.409347	0.000000
TIME TAKEN WAS 12.62MINS			
0.00	0.264276	-4.409351	-0.000004 0.2672770E-13
0.04	0.272430	-5.011090	-0.080378 0.1131535E-11
0.08	0.280178	-5.566283	-0.114205 0.7453490E-12
0.12	0.287551	-6.108745	-0.135302 0.4985994E-12
0.16	0.294576	-6.645097	-0.150289 0.3383239E-12
0.20	0.301280	-7.178215	-0.162042 0.2324811E-12
0.24	0.307686	-7.709570	-0.172031 0.1621667E-12
0.28	0.313816	-8.239768	-0.181064 0.1146660E-12
0.32	0.319689	-8.769854	-0.189584 0.8211872E-13
0.36	0.325325	-9.299447	-0.197812 0.5953132E-13
0.40	0.330739	-9.828820	-0.205820 0.4366033E-13
0.44	0.335946	-10.357941	-0.213575 0.3238550E-13
0.48	0.340960	-10.886696	-0.220965 0.2426699E-13
0.52	0.345792	-11.414903	-0.227807 0.1836113E-13
0.56	0.350455	-11.942314	-0.233853 0.1400697E-13
0.60	0.354959	-12.468616	-0.238789 0.1079513E-13
0.64	0.359313	-12.993419	-0.242227 0.8382130E-14
0.68	0.363525	-13.516245	-0.243688 0.6556333E-14
0.72	0.367605	-14.036493	-0.242571 0.5187636E-14
0.76	0.371559	-14.553399	-0.238111 0.4107771E-14
0.80	0.375394	-15.065950	-0.229297 0.3294186E-14
0.84	0.379116	-15.572746	-0.214728 0.2612439E-14
0.88	0.382731	-16.071676	-0.192293 0.9707463E-08
0.92	0.386245	-16.559200	-0.158451 0.8905985E-08
0.96	0.389662	-17.027957	-0.105843 0.8180794E-08
1.00	0.392984	-17.443479	0.000000

31-JAN-77

32POINTS AT INTERVALS OF 0.195

DENSITY= 0.379RATIO OF DIPOLES= 1.50RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1600 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.250879	-3.829366	0.000000
TIME TAKEN WAS 12.72MINS			
0.00	0.250879	-3.829369	-0.000003 0.1445019E-13
0.04	0.259229	-4.388173	-0.083081 0.1527491E-11
0.08	0.267167	-4.900145	-0.119327 0.1001886E-11
0.12	0.274722	-5.399108	-0.142563 0.6661685E-12
0.16	0.281920	-5.891698	-0.159428 0.4485725E-12
0.20	0.288789	-6.380799	-0.172803 0.3060195E-12
0.24	0.295352	-6.867889	-0.184167 0.2118097E-12
0.28	0.301631	-7.353783	-0.194335 0.1485868E-12
0.32	0.307646	-7.838933	-0.203759 0.1056121E-12
0.36	0.313417	-8.323565	-0.212664 0.7600252E-13
0.40	0.318958	-8.807759	-0.221133 0.5534630E-13
0.44	0.324287	-9.291490	-0.229138 0.4077549E-13
0.48	0.329417	-9.774650	-0.236572 0.3034676E-13
0.52	0.334361	-10.257064	-0.243260 0.2282023E-13
0.56	0.339130	-10.738489	-0.248959 0.1731856E-13
0.60	0.343735	-11.218618	-0.253362 0.1326711E-13
0.64	0.348186	-11.697067	-0.256085 0.1025650E-13
0.68	0.352491	-12.173361	-0.256653 0.7977072E-14
0.72	0.356660	-12.646908	-0.254473 0.6277910E-14
0.76	0.360699	-13.116944	-0.248784 0.4956051E-14
0.80	0.364617	-13.582465	-0.238579 0.3924758E-14
0.84	0.368418	-14.042067	-0.222455 0.3169286E-14
0.88	0.372110	-14.493655	-0.198317 0.2542183E-14
0.92	0.375698	-14.933692	-0.162628 0.9491874E-08
0.96	0.379186	-15.354822	-0.108032 0.8713067E-08
1.00	0.382577	-15.722516	0.000000

31-JAN-77

32POINTS AT INTERVALS OF 0.184

DENSITY= 0.369RATIO OF DIPOLES= 1.50RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1700 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.237919	-3.335199	0.000000
TIME TAKEN WAS	12.85MINS		
0.00	0.237919	-3.335201	-0.000002
0.04	0.246461	-3.856436	-0.085403
0.08	0.254585	-4.330598	-0.123730
0.12	0.262321	-4.791517	-0.148814
0.16	0.269692	-5.245841	-0.167303
0.20	0.276726	-5.696457	-0.182086
0.24	0.283446	-6.144852	-0.194645
0.28	0.289875	-6.591846	-0.205805
0.32	0.296033	-7.037896	-0.216020
0.36	0.301938	-7.483234	-0.225524
0.40	0.307608	-7.927947	-0.234403
0.44	0.313059	-8.372013	-0.242634
0.48	0.318305	-8.815331	-0.250118
0.52	0.323359	-9.257729	-0.256681
0.56	0.328234	-9.698970	-0.262088
0.60	0.332940	-10.138751	-0.266034
0.64	0.337487	-10.576693	-0.268142
0.68	0.341886	-11.012327	-0.267940
0.72	0.346143	-11.445061	-0.264840
0.76	0.350267	-11.874139	-0.258084
0.80	0.354266	-12.298558	-0.246668
0.84	0.358147	-12.716920	-0.229196
0.88	0.361914	-13.127128	-0.203570
0.92	0.365575	-13.525659	-0.166266
0.96	0.369133	-13.905177	-0.109949
1.00	0.372593	-14.231062	0.000000

31-JAN-77

32POINTS AT INTERVALS OF 0.174

DENSITY= 0.359RATIO OF DIPOLES= 1.50RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1800 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.225345	-2.911337	0.000000
TIME TAKEN WAS	12.82MINS		
0.00	0.225345	-2.911337	-0.000001
0.04	0.234071	-3.399416	-0.087396
0.08	0.242379	-3.840212	-0.127509
0.12	0.250293	-4.267579	-0.154193
0.16	0.257838	-4.688157	-0.174087
0.20	0.265037	-5.104843	-0.190091
0.24	0.271915	-5.519128	-0.203693
0.28	0.278494	-5.931838	-0.215719
0.32	0.284795	-6.343433	-0.226631
0.36	0.290836	-6.754149	-0.236664
0.40	0.296635	-7.164077	-0.245909
0.44	0.302209	-7.573200	-0.254349
0.48	0.307571	-7.981420	-0.261885
0.52	0.312737	-8.388568	-0.268351
0.56	0.317717	-8.794413	-0.273512
0.60	0.322524	-9.198654	-0.277070
0.64	0.327168	-9.600917	-0.278650
0.68	0.331659	-10.000734	-0.277784
0.72	0.336005	-10.397520	-0.273886
0.76	0.340214	-10.790520	-0.266204
0.80	0.344294	-11.178736	-0.253736
0.84	0.348253	-11.560771	-0.235088
0.88	0.352095	-11.934533	-0.208167
0.92	0.355828	-12.296499	-0.169450
0.96	0.359455	-12.639350	-0.111618
1.00	0.362984	-12.928415	0.000000

31-JAN-77

32POINTS AT INTERVALS OF 0.164

DENSITY= 0.350 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= -0.1900 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.213114	-2.545740	0.000000
TIME TAKEN WAS	12.95MINS		
0.00	0.213114	-2.545740	-0.000001 0.7187718E-15
0.04	0.222015	-3.004327	-0.089105 0.3725977E-11
0.08	0.230501	-3.415460	-0.130756 0.2460744E-11
0.12	0.238592	-3.812996	-0.158810 0.1624387E-11
0.16	0.246309	-4.203586	-0.179918 0.1077933E-11
0.20	0.253675	-4.590131	-0.196980 0.7217160E-12
0.24	0.260712	-4.974123	-0.211489 0.4887032E-12
0.28	0.267442	-5.356390	-0.224274 0.3349750E-12
0.32	0.273887	-5.737396	-0.235798 0.2325340E-12
0.36	0.280065	-6.117381	-0.246301 0.1634642E-12
0.40	0.285994	-6.496437	-0.255875 0.1163552E-12
0.44	0.291691	-6.874551	-0.264506 0.8382742E-13
0.48	0.297172	-7.251627	-0.272100 0.6108260E-13
0.52	0.302449	-7.627500	-0.278491 0.4501298E-13
0.56	0.307536	-8.001941	-0.283450 0.3351827E-13
0.60	0.312445	-8.374653	-0.286679 0.2518900E-13
0.64	0.317185	-8.745263	-0.287807 0.1913568E-13
0.68	0.321768	-9.113308	-0.286369 0.1465402E-13
0.72	0.326203	-9.478204	-0.281783 0.1131815E-13
0.76	0.330497	-9.839200	-0.273297 0.8807137E-14
0.80	0.334659	-10.195299	-0.259914 0.6898074E-14
0.84	0.338695	-10.545110	-0.240242 0.5471264E-14
0.88	0.342613	-10.886541	-0.212191 0.4349765E-14
0.92	0.346418	-11.216073	-0.172242 0.3465056E-14
0.96	0.350114	-11.526391	-0.113077 0.2800657E-14
1.00	0.353710	-11.782796	0.000000

29-JAN-77

32POINTS AT INTERVALS OF 0.195

DENSITY= 0.375 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.010

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1600 ET PRESSURE= 0.001383

X	DENSITY	GMIXTURE	GMIXING
0.00	0.235110	-3.460270	0.000000
TIME TAKEN WAS	13.03MINS		
0.00	0.235110	-3.460272	-0.000002 0.1132395E-13
0.04	0.244806	-4.010912	-0.078150 0.8075834E-11
0.08	0.253902	-4.515704	-0.110451 0.4468229E-11
0.12	0.262462	-5.008303	-0.130558 0.2570726E-11
0.16	0.270537	-5.495214	-0.144978 0.1530021E-11
0.20	0.278177	-5.979214	-0.156486 0.9390185E-12
0.24	0.285422	-6.461695	-0.166475 0.5930548E-12
0.28	0.292309	-6.943405	-0.175693 0.3841702E-12
0.32	0.298867	-7.424736	-0.184533 0.2546436E-12
0.36	0.305126	-7.905870	-0.193176 0.1723288E-12
0.40	0.311109	-8.386847	-0.201661 0.1188477E-12
0.44	0.316837	-8.867608	-0.209930 0.8339390E-13
0.48	0.322331	-9.348018	-0.217849 0.5944735E-13
0.52	0.327608	-9.827876	-0.225216 0.4298092E-13
0.56	0.332682	-10.306922	-0.231770 0.3149271E-13
0.60	0.337567	-10.784828	-0.237184 0.2337160E-13
0.64	0.342277	-11.261197	-0.241062 0.1752992E-13
0.68	0.346822	-11.735540	-0.242914 0.1329980E-13
0.72	0.351212	-12.207252	-0.242134 0.1017816E-13
0.76	0.355458	-12.675562	-0.237952 0.7870983E-14
0.80	0.359568	-13.139452	-0.229350 0.6136259E-14
0.84	0.363549	-13.597514	-0.214921 0.4830880E-14
0.88	0.367409	-14.047643	-0.192558 0.3824740E-14
0.92	0.371154	-14.486298	-0.158722 0.3019828E-14
0.96	0.374790	-14.906118	-0.106051 0.2419614E-14
1.00	0.378320	-15.272559	0.000000

29-JAN-77

32POINTS AT INTERVALS OF 0.174

DENSITY= 0.364RATIO OF DIPOLES= 1.5ORATIO OF RADII=1.000

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1800 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.225345	-2.911336	0.000000
TIME TAKEN WAS	9.63MINS		
0.00	0.225345	-2.911337	-0.000001
0.04	0.234470	-3.413754	-0.076641
0.08	0.243150	-3.870158	-0.107268
0.12	0.251408	-4.314291	-0.125625
0.16	0.259269	-4.752772	-0.138329
0.20	0.266760	-5.188422	-0.148203
0.24	0.273906	-5.622675	-0.156679
0.28	0.280731	-6.056307	-0.164534
0.32	0.287258	-6.489734	-0.172184
0.36	0.293508	-6.923150	-0.179824
0.40	0.299499	-7.356609	-0.187506
0.44	0.305249	-7.790059	-0.195179
0.48	0.310775	-8.223371	-0.202715
0.52	0.316091	-8.656349	-0.209916
0.56	0.321211	-9.088733	-0.216524
0.60	0.326146	-9.520200	-0.222214
0.64	0.330909	-9.950352	-0.226589
0.68	0.335509	-10.378701	-0.229162
0.72	0.339957	-10.804642	-0.229326
0.76	0.344260	-11.227403	-0.226310
0.80	0.348428	-11.645967	-0.219098
0.84	0.352467	-12.058924	-0.206278
0.88	0.356385	-12.464165	-0.185743
0.92	0.360187	-12.858155	-0.153956
0.96	0.363879	-13.233559	-0.103584
1.00	0.367467	-13.555752	0.000000

29-JAN-77

32POINTS AT INTERVALS OF 0.164

DENSITY= 0.355RATIO OF DIPOLES= 1.5ORATIO OF RADII=1.000

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.1900 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.213114	-2.545740	0.000000
TIME TAKEN WAS	9.63MINS		
0.00	0.213114	-2.545740	-0.000001
0.04	0.222417	-3.017229	-0.078765
0.08	0.231279	-3.442484	-0.111297
0.12	0.239718	-3.855258	-0.131348
0.16	0.247757	-4.262180	-0.145546
0.20	0.255419	-4.666076	-0.156718
0.24	0.262729	-5.068385	-0.166304
0.28	0.269711	-5.469888	-0.175083
0.32	0.276387	-5.871005	-0.183476
0.36	0.282778	-6.271935	-0.191683
0.40	0.288904	-6.672735	-0.199759
0.44	0.294782	-7.073358	-0.207659
0.48	0.300428	-7.473679	-0.215256
0.52	0.305860	-7.873504	-0.222358
0.56	0.311089	-8.272579	-0.228709
0.60	0.316128	-8.670583	-0.233990
0.64	0.320990	-9.067123	-0.237806
0.68	0.325686	-9.461715	-0.239674
0.72	0.330224	-9.853755	-0.238991
0.76	0.334614	-10.242477	-0.234989
0.80	0.338865	-10.626867	-0.226655
0.84	0.342984	-11.005516	-0.212581
0.88	0.346978	-11.376322	-0.190663
0.92	0.350854	-11.735749	-0.157367
0.96	0.354616	-12.076474	-0.105368
1.00	0.358273	-12.363829	0.000000

29-JAN-77

32POINTS AT INTERVALS OF 0.156

DENSITY= 0.346 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.000

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.2000 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.201196	-2.228936	0.000000
TIME TAKEN WAS	9.80MINS		
0.00	0.201196	-2.228936	-0.000000 0.1614919E-15
0.04	0.210660	-2.672728	-0.080600 0.1212740E-13
0.08	0.219696	-3.070096	-0.114775 0.4743698E-11
0.12	0.228313	-3.454806	-0.136292 0.3123712E-11
0.16	0.236528	-3.833492	-0.151787 0.2052926E-11
0.20	0.244362	-4.208988	-0.164090 0.1355591E-11
0.24	0.251838	-4.582735	-0.174645 0.9029738E-12
0.28	0.258978	-4.955519	-0.184236 0.6081641E-12
0.32	0.265805	-5.327762	-0.193286 0.4146691E-12
0.36	0.272339	-5.699666	-0.201998 0.2863720E-12
0.40	0.278600	-6.071291	-0.210430 0.2003193E-12
0.44	0.284607	-6.442592	-0.218539 0.1418977E-12
0.48	0.290377	-6.813447	-0.226201 0.1017580E-12
0.52	0.295924	-7.183666	-0.233228 0.7383151E-13
0.56	0.301263	-7.552996	-0.239366 0.5417232E-13
0.60	0.306408	-7.921122	-0.244299 0.4017874E-13
0.64	0.311371	-8.287650	-0.247635 0.3010260E-13
0.68	0.316161	-8.652101	-0.248893 0.2277513E-13
0.72	0.320791	-9.013874	-0.247474 0.1737841E-13
0.76	0.325268	-9.372205	-0.242613 0.1337727E-13
0.80	0.329603	-9.726083	-0.233298 0.1037966E-13
0.84	0.333801	-10.074103	-0.218126 0.8117584E-14
0.88	0.337872	-10.414164	-0.194994 0.6408882E-14
0.92	0.341822	-10.742735	-0.160373 0.5083553E-14
0.96	0.345654	-11.052491	-0.106936 0.4040117E-14
1.00	0.349380	-11.308747	0.000000

29-JAN-77

32POINTS AT INTERVALS OF 0.104

DENSITY= 0.267 RATIO OF DIPOLES= 1.50 RATIO OF RADII=1.000

8POINT QUAD 6POINTS FOR INTERP GIVEN 32

TEMP= 0.3000 ET PRESSURE= 0.002535

X	DENSITY	GMIXTURE	GMIXING
0.00	0.101143	-0.605709	0.000000
TIME TAKEN WAS	10.40MINS		
0.00	0.101143	-0.605709	0.000000 0.3848918E-17
0.04	0.108858	-0.877727	-0.091622 0.2947286E-08
0.08	0.117181	-1.100861	-0.134361 0.4950618E-08
0.12	0.125916	-1.309612	-0.162715 0.7117463E-08
0.16	0.134857	-1.511123	-0.183831 0.8916687E-08
0.20	0.143819	-1.708554	-0.200866 0.2001432E-13
0.24	0.152664	-1.903529	-0.215445 0.1938852E-13
0.28	0.161297	-2.096928	-0.228447 0.1654357E-13
0.32	0.169661	-2.289209	-0.240333 0.9404444E-08
0.36	0.177727	-2.480586	-0.251314 0.8555232E-08
0.40	0.185483	-2.671108	-0.261440 0.3877702E-11
0.44	0.192931	-2.860713	-0.270649 0.2601216E-11
0.48	0.200079	-3.049263	-0.278803 0.1736797E-11
0.52	0.206939	-3.236553	-0.285697 0.1162778E-11
0.56	0.213525	-3.422317	-0.291065 0.7840581E-12
0.60	0.219852	-3.606228	-0.294580 0.5338889E-12
0.64	0.225935	-3.787888	-0.295845 0.3676403E-12
0.68	0.231788	-3.966812	-0.294372 0.2562082E-12
0.72	0.237425	-4.142398	-0.289562 0.1807338E-12
0.76	0.242859	-4.313882	-0.280650 0.1290404E-12
0.80	0.248102	-4.480254	-0.266627 0.9321358E-13
0.84	0.253165	-4.640115	-0.246091 0.6809738E-13
0.88	0.258059	-4.791368	-0.216949 0.5029999E-13
0.92	0.262794	-4.930487	-0.175671 0.3752722E-13
0.96	0.267378	-5.050100	-0.114888 0.2824992E-13
1.00	0.271821	-5.115607	0.000000