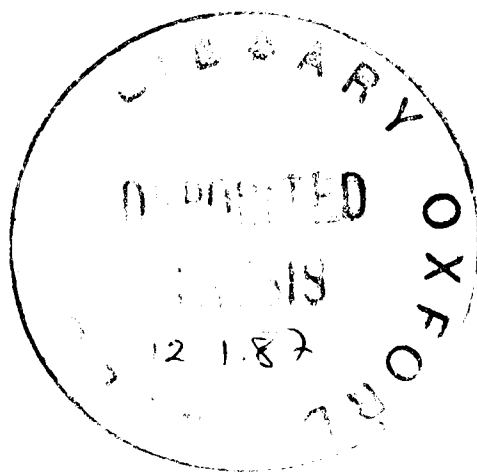


*PHASE SEPARATION IN SOLUTIONS OF LARGE
SPHERICAL PARTICLES*

by

George Jackson



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Doctor of Philosophy
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ABSTRACT

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The effect of large size ratios of solute to solvent on the critical properties and phase behaviour of binary mixtures of spherical particles is investigated using an "augmented van der Waals" equation of state. The equation used is essentially a van der Waals equation with an improved hard sphere repulsive term.

Molecular dynamics and constant-pressure Monte Carlo simulations of binary mixtures of hard spheres with different diameter ratios and mole fractions are undertaken to check the adequacy of the hard sphere equation. Good agreement is found, even for systems with large differences in size. Furthermore, many of the hard sphere mixtures exhibited a transition from a fluid to a solid phase at high densities.

Phase boundaries are calculated for model mixtures comprising spheres of different sizes between which there are long-ranged attractive forces. Particular attention is paid to the case in which the ratio of sizes is infinite. The systems show a wide variety of behaviour that includes liquid-liquid and gas-gas immiscibility, and the formation of negative azeotropes. Calculations investigating the effect of different attractive interactions between the small and large spheres show that as the magnitude of this interaction is increased, liquid-liquid immiscibility becomes the dominant feature of the phase diagram at moderate temperatures. The extent of liquid-liquid coexistence is greatest at large size differences. These model systems are shown to reproduce some of the behaviour of aqueous solutions of surfactants if it is assumed that the large spheres are models of the micelles and the small spheres models of the solvent molecules.

The properties of binary lattice mixtures of bifunctional molecules whose ends are chosen to mimic surfactant and solvent molecules are also briefly investigated, to determine the effect of the asymmetric surfactant molecule on the phase separation. Closed-loops emerge in the phase diagrams as the surfactant character of one of the species is increased.

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CHAPTER 1

HARD SPHERES AND THEIR MIXTURES

1.1 INTRODUCTION

Colloidal dispersions, micellar solutions and other such systems, which comprise solute particles that are large relative to the solvent particles in which they are dispersed, are an ever increasing feature of everyday life. Indeed, the principal components of these complex systems are of considerable industrial interest, appearing commercially as emulsifiers, detergents and solubilizers etc. The physical and chemical properties of these solutions seem to be dominated by the large solute-to-solvent size ratios. They exhibit very interesting phase behaviour with varying degrees of immiscibility, including such complex phenomena as Lower Critical Solution Temperatures (LCST) at low solute densities, as well as closed coexistence loops.

Very often, for solutions of such systems, the solute may be approximated by spherical particles in some regions of the phase diagram, and in certain cases this may be true even over a relatively large temperature and concentration

range: NMR line-width and diffusion studies for zwitterionic betaine sulphate surfactant-water systems indicate that small spherical micelles are formed which show no dramatic growth in aggregate size with changes in temperature and concentration [1]; in aqueous micellar solutions of polyoxyethylene surfactants ($C_{12}E_8$), the small spherical micelles are not appreciably affected by changes in temperature and are thought to remain virtually unchanged in size and shape for a range of concentrations [2],[3]. Bearing in mind these experimental observations, a possible approximation for these solutions could involve an equation of state for mixtures of rigid spheres.

The effect of large size ratios on the phase separation of binary mixtures of spherical particles has received little attention in the literature. The Flory-Huggins polymer solution theory [4] treats size differences specifically in terms of polymer linkages and ideal behaviour. Van Konynenburg and Scott [5] have determined the critical lines and phase equilibria of binary van der Waals mixtures over a range of attractive interactions for equal particle diameters $d_1=d_2$ as well as some results for $d_2/d_1=1.26$. However, in the case of micellar solutions and colloidal dispersions much larger solute-to-solvent size ratios are encountered. In order to investigate the mechanisms of phase separation in such systems, this thesis presents theoretical studies of phase equilibria in binary mixtures of spheres with large diameter ratios (eg. $d_2/d_1=20/1$ and $d_2/d_1=\infty$).

In this chapter the suitable equations of state for hard sphere mixtures are discussed, and the equation which is the the best representation of the hard sphere properties is chosen. The equation of state's adequacy in reproducing the exact hard sphere data is established in Chapter 2. Monte Carlo and molecular dynamics simulations are undertaken for binary mixtures of hard spheres of different sizes and compositions, and the results are compared with those calculated using the hard sphere equation. In Chapter 3 the critical point and phase equilibria of a system of pure hard cores is determined. Throughout the research the term "hard cores" will refer to systems of hard spheres between which there are weak but long-ranged attractive interactions. An investigation of the phase equilibria in binary mixtures of hard cores with large size differences is undertaken for systems of point particles and spheres in Chapter 4, and for systems with large but finite size ratios in Chapter 5. Chapter 6 compares these results with the equivalent calculations for mixtures of point particles and van der Waals molecules. Some phase separations in mixtures distributed on a lattice are also presented in Chapter 7 for a binary mixture of A-A, solvent molecules, and a-b, surfactant molecules, to investigate the effect of the asymmetric surfactant molecule on the phase separation. Finally, Chapter 8 compares the results of the theoretical calculations with experimental data for aqueous solutions of surfactants.

1.2 EQUATION OF STATE FOR PURE HARD SPHERES

Systems of hard spheres are of interest in statistical mechanics because they provide a starting point for perturbation theories applicable to more realistic intermolecular potentials, as well as being one of the simplest systems to exhibit freezing transitions. An accurate representation of an assembly of pure rigid spheres was proposed by Carnahan and Starling [6]. Carnahan and Starling approximated the reduced virial coefficients of an accurate reduced virial expansion, obtained from known virial coefficients, by integers to give an infinite power series which on summing produced the familiar form of the equation of state for the compression factor Z in terms of the reduced density η .

$$Z^{CS} = \frac{PV}{NkT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad \eta = \frac{\pi N d^3}{6V}$$

This equation can be understood as an averaging process over the compressibility and virial results from the solution of the Percus-Yevick (PY) integral equation [7]. This integral equation for the radial distribution function was solved explicitly for pure hard spheres by Thiele [8] and by Wertheim [9]. Two routes are then possible to an equation of state: the compressibility equation requires the grand canonical ensemble for its derivation and the virial equation relates the pressure to the pair

distribution function by differentiation of the logarithm of the configurational integral of the canonical ensemble.

$$Z^c = \frac{1+\eta+\eta^2}{(1-\eta)^3} \qquad Z^v = \frac{1+2\eta+3\eta^2}{(1-\eta)^2}$$

Neither of these equations exhibit a phase transition whereas the computer simulations show that rigid spheres solidify at high densities. Furthermore, these equations permit densities in excess of close-packing, $\eta=\pi\sqrt{2}/6$. However, in the fluid region both the compressibility and, to a lesser degree, the virial expressions are in close agreement with machine simulations (Fig. 2.1 of Chapter 2).

Carnahan and Starling observed that taking one third of the virial result and adding to it two thirds of the compressibility result reproduces the equation obtained from the accurate virial expansion.

$$Z^{CS} = \frac{2}{3} Z^c + \frac{1}{3} Z^v$$

This relation is in excellent agreement with machine-calculated results for pure hard sphere systems, and, rather surprisingly, the equation is superior in accuracy to the Padé approximant virial expansion on which it is based [6]. In Section 2.3 of Chapter 2 the Carnahan and Starling equation is compared with the exact data obtained from molecular dynamics simulations.

1.3 EQUATIONS OF STATE FOR HARD SPHERE MIXTURES

1.3.1 Mansoori Equation

The Percus-Yevick integral equation for mixtures of hard spheres was solved explicitly by Lebowitz [10]. Mansoori et al. [11] generalized the approach of Carnahan and Starling to mixtures by using Lebowitz's results to give an accurate representation of hard sphere mixtures. As expected the resulting equation of state, and thermodynamic functions calculated from it, reproduce the computer-calculated data for mixtures of hard spheres very well at liquid densities, but it fails to predict the solid transitions (see Chapter 2). The Mansoori equation is based on an averaging process over the compressibility and virial results and it is the best analytical equation of state presently available for multicomponent systems of rigid spheres.

Lebowitz's results for a hard sphere mixture of m components are

$$Z^C = \frac{(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi)}{(1 - \xi)^3}$$

$$Z^V = Z^C - \frac{3\xi^3 y_3}{(1 - \xi)^3}$$

with

$$\xi = \sum_{i=1}^m \eta_i, \quad \eta_i = \frac{\pi N_i d_i^3}{6V}, \quad \sum_{i=1}^m x_i = 1$$

$$y_1 = \sum_{j>1}^m \Delta_{ij} (d_i + d_j) (d_i d_j)^{-1/2}$$

$$y_2 = \sum_{j>1}^m \Delta_{ij} \sum_{k=1}^m \left(\frac{\eta_k}{\xi} \right) \frac{(d_i d_j)^{1/2}}{d_k}$$

$$y_3 = \left[\sum_{i=1}^m \left(\frac{\eta_i}{\xi} \right)^{2/3} x_i^{1/3} \right]^3$$

$$\Delta_{ij} = [(\eta_i \eta_j)^{1/2} / \xi] [(d_i - d_j)^2 / d_i d_j] (x_i x_j)^{1/2}$$

where $Z = PV/NkT$ is the compression factor and ξ the total reduced density. η_i is the reduced density, d_i the hard sphere diameter and x_i the mole fraction of the i^{th} component. By taking the appropriate average the Mansoori equation follows:

$$Z^{cv} = \frac{2}{3} Z^c + \frac{1}{3} Z^v$$

$$Z^{cv} = \frac{(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi) - y_3\xi^3}{(1 - \xi)^3}$$

This average is in agreement with theoretical calculations by Lebowitz and Rowlinson [12] for mixtures of hard spheres which indicate the superiority of the compressibility relation over the virial result.

In the case of a binary mixture of the hard spheres the Mansoori equation becomes

$$Z^{cv} = \frac{(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi) - y_3\xi^3}{(1 - \xi)^3}$$

$$\xi = \sum_{i=1}^2 \eta_i = \eta_1 + \eta_2, \quad \eta_1 = \frac{\pi N_1 d_1^3}{6V}, \quad \eta_2 = \frac{\pi N_2 d_2^3}{6V}$$

$$y_1 = \frac{(d_1 - d_2)^2 (d_1 + d_2) x_1 x_2}{(d_1^3 x_1 + d_2^3 x_2)}, \quad y_3 = \frac{(d_1^2 x_1 + d_2^2 x_2)^3}{(d_1^3 x_1 + d_2^3 x_2)^2}$$

$$y_2 = \frac{d_1 d_2 (d_1 - d_2)^2 (d_1^2 x_1 + d_2^2 x_2) x_1 x_2}{(d_1^3 x_1 + d_2^3 x_2)^2}$$

1.3.2 McGlashan Equation

A similar but not identical equation of state for a mixture of hard spheres has been used for phase equilibrium calculations by McGlashan et al. [13]. McGlashan started with the equation of state for pure rigid spheres obtained by Carnahan and Starling which is expressed in terms of the molar volume, V_m , and the sphere size parameter, b , (instead of the reduced density which incorporates both these parameters) plus a van der Waals type attractive term, involving the parameter a .

$$P = RT \frac{V_m^3 + V_m^2 b + V_m b^2 - b^3}{V_m (V_m - b)^3} - \frac{a}{V_m^2}, \quad b = \frac{\pi L d^3}{6}$$

The equation was then extended to binary fluid mixtures by using the "one-fluid" theory of mixtures, redefining the intrinsic volume parameter b and the attractive parameter a with those prescribed by van der Waals.

$$b = b_{11}x_1^2 + 2b_{12}x_1x_2 + b_{22}x_2^2, \quad b_{12}^{1/3} = \frac{1}{2}(b_{11}^{1/3} + b_{22}^{1/3})$$

$$a = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2$$

This is an appropriate approximation in the case of non-polar, non-reacting components removed from the critical

point when there are no large differences between the critical temperatures and molecular sizes of the pure components. Hence, one would expect the hard sphere repulsive term of this approximate equation, derived from the pure hard sphere Carnahan-Starling relation, to be a less accurate representation of a hard sphere mixture's properties than the Mansoori et al. equation described earlier. This point is pursued in the following section.

1.4 VIRIAL COEFFICIENTS

A formal comparison of the Mansoori and McGlashan expressions for binary mixtures of hard spheres can be achieved by comparing their corresponding virial coefficients with the exact hard sphere virial coefficients.

1.4.1 Mansoori Virial Coefficients

By using the binomial expansion, the Mansoori et al. equation of state is expressed in terms of a power series in density.

$$Z^{CV} = [(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi) - y_3\xi^3] (1 + 3\xi + 6\xi^2 + \dots)$$

$$Z^{CV} = 1 + (4 - 3y_1)\xi + (10 - 9y_1 - 3y_2)\xi^2 + \dots$$

The second virial coefficient (B) is the coefficient of the linear terms in density, and the third virial coefficient (C) is the coefficient of terms in density squared.

$$B^{cv} = V (4-3y_1) \xi$$

$$C^{cv} = V^2 (10-9y_1-3y_2) \xi^2$$

with

$$y_1 = \frac{(d_1-d_2)^2 (d_1+d_2) x_1 x_2}{(d_1^3 x_1 + d_2^3 x_2)}$$

$$y_2 = \frac{d_1 d_2 (d_1-d_2)^2 (d_1^2 x_1 + d_2^2 x_2) x_1 x_2}{(d_1^3 x_1 + d_2^3 x_2)^2}$$

The second virial coefficient is

$$B^{cv} = \frac{2}{3} \pi N \left[d_1^3 x_1^2 + 2 \left(\frac{d_1+d_2}{2} \right)^3 x_1 x_2 + d_2^3 x_2^2 \right]$$

The third virial coefficient is

$$C^{cv} = \frac{5}{8} \left(\frac{2}{3} \pi N d_1^3 \right)^2 x_1^3 + \frac{5}{8} \left(\frac{2}{3} \pi N d_2^3 \right)^2 x_2^3$$

$$+ \frac{3}{54} \pi^2 N^2 \left[d_1^6 + 32 \left(\frac{d_1+d_2}{2} \right)^3 d_1^3 - 18 \left(\frac{d_1+d_2}{2} \right)^2 d_1^4 \right] x_1^2 x_2$$

$$+ \frac{3}{54} \pi^2 N^2 \left[d_2^6 + 32 \left(\frac{d_1+d_2}{2} \right)^3 d_2^3 - 18 \left(\frac{d_1+d_2}{2} \right)^2 d_2^4 \right] x_1 x_2^2$$

Therefore, it is clear that the virial coefficients have the expected form:

$$B = B_{11}x_1^2 + 2B_{12}x_1x_2 + B_{22}x_2^2$$

$$C = C_{111}x_1^3 + 3C_{112}x_1^2x_2 + 3C_{122}x_1x_2^2 + C_{222}x_2^3$$

1.4.2 Exact Hard Sphere Virial Coefficients

Kihara [14] has calculated the second and third virial coefficients for various systems of unlike molecules including square well and Lennard-Jones potentials using the expressions for the coefficients derived from statistical mechanics (these can be explicitly integrated for such systems). The results obtained for a binary mixture of square wells were particularly helpful in our case because by taking the well depth as zero, a hard sphere potential is obtained with corresponding expressions for the virial coefficients. Hence, the exact second and third virial coefficients for a binary mixture of hard spheres derived from Kihara's square well expressions are quoted as follows:

$$B_{11} = \frac{2}{3}\pi Nd_1^3, \quad B_{22} = \frac{2}{3}\pi Nd_2^3, \quad B_{12} = \frac{2}{3}\pi N \left(\frac{d_1 + d_2}{2} \right)^3$$

$$C_{111} = \frac{5}{8} \left(\frac{2}{3}\pi Nd_1^3 \right)^2, \quad C_{222} = \frac{5}{8} \left(\frac{2}{3}\pi Nd_2^3 \right)^2$$

$$C_{112} = \frac{1}{54}\pi^2 N^2 \left[d_1^6 + 32 \left(\frac{d_1 + d_2}{2} \right)^3 d_1^3 - 18 \left(\frac{d_1 + d_2}{2} \right)^2 d_1^4 \right]$$

$$C_{122} = \frac{1}{54}\pi^2 N^2 \left[d_2^6 + 32 \left(\frac{d_1 + d_2}{2} \right)^3 d_2^3 - 18 \left(\frac{d_1 + d_2}{2} \right)^2 d_2^4 \right]$$

The above results are reproduced by the Mansoori et al. equation of state, indicating that this hard sphere equation is correct to the third virial coefficient. This result is not unexpected because the equation is based on the Percus-Yevick approximation which is correct to three-centre interactions but neglects some four-centre interactions. In fact, if the pure Carnahan-Starling hard sphere equation is expanded in a similar fashion, the fourth virial coefficient is obtained and it is found to be slightly different to the exact hard sphere result (see below).

$$D^{CV} = \frac{1}{12}\pi^3 N^3 d^9 = \frac{9}{32}b^3 = 0.28125b^3, \quad b = \frac{2}{3}\pi Nd^3$$

$$D^{exact} = 0.28695b^3$$

Therefore, the Carnahan-Starling hard sphere equation is not correct to the fourth virial coefficient but has a small error of 1.97% in D .

1.4.3 McGlashan Virial Coefficients

The virial coefficients for the equation proposed by McGlashan et al. are obtained in much the same way. If the repulsive portion of the equation is expanded, an appropriate power series in density is obtained from which the virial coefficients are determined (Note that the parameter b in the equation is equivalent to the corresponding van der Waals parameter b' , with $b'=4b$).

$$\begin{aligned}\frac{PV_m}{RT} &= \left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} - \frac{b^3}{V_m^3} \right) \left(1 + 3 \frac{b}{V_m} + 6 \frac{b^2}{V_m^2} + \dots \right) \\ &= 1 + 4 \frac{b}{V_m} + 10 \frac{b^2}{V_m^2} + \dots\end{aligned}$$

with

$$\begin{aligned}b &= b'/4, \quad b' = b_{11}x_1^2 + 2b_{12}x_1x_2 + b_{22}x_2^2 \\ b_{11} &= \frac{2}{3}\pi L d_1^3, \quad b_{22} = \frac{2}{3}\pi L d_2^3, \quad b_{12} = [(b_{11}^{1/3} + b_{22}^{1/3})/2]^3\end{aligned}$$

The second molar virial coefficient is

$$\begin{aligned}B^{\text{McG}} &= 4b = b' \\ B^{\text{McG}} &= \frac{2}{3}\pi L \left[d_1^3 x_1^2 + 2 \left(\frac{d_1 + d_2}{2} \right)^3 x_1 x_2 + d_2^3 x_2^2 \right]\end{aligned}$$

The third molar virial coefficient is

$$\begin{aligned}C^{\text{McG}} &= 10b^2 = \frac{5}{8}b'^2 \\ C^{\text{McG}} &= \frac{5}{8} \left(\frac{2}{3}\pi L d_1^3 \right)^2 x_1^3 + \frac{5}{8} \left(\frac{2}{3}\pi L d_2^3 \right)^2 x_2^3 \\ &\quad + \frac{5}{36}\pi^2 L^2 \left(-d_1^6 + 3d_1^5 d_2 + 3d_1^4 d_2^2 + d_1^3 d_2^3 \right) x_1^2 x_2 \\ &\quad + \frac{5}{32}\pi^2 L^2 \left(d_1^6 - 2d_1^5 d_2 - d_1^4 d_2^2 + 4d_1^3 d_2^3 - d_1^2 d_2^4 - 2d_1 d_2^5 + d_2^6 \right) x_1^2 x_2^2 \\ &\quad + \frac{5}{36}\pi^2 L^2 \left(-d_2^6 + 3d_2^5 d_1 + 3d_2^4 d_1^2 + d_2^3 d_1^3 \right) x_2^2 x_1\end{aligned}$$

It is clear that the second virial coefficient is the same as the exact virial coefficient whilst the third virial coefficient differs from it. In order to quantify this deviation from the exact result, we can examine the difference between the exact and the McGlashan third virial (shown below).

$$\Delta C = \frac{1}{96} \pi^2 L^2 (d_1 - d_2)^2 \left[8d_1^3 (2d_1 + d_2) x_1 - 15 (d_1^2 - d_2^2)^2 x_1 x_2 + 8d_2^3 (2d_2 + d_1) x_2 \right] x_1 x_2$$

It is interesting to note that the greater the difference in the molecular sizes of the two components, the more the McGlashan equation's third virial coefficient deviates from the exact result. This observation confirms that the "one-fluid" approximation mentioned previously does not hold true when the two components vary in size. In the case of a binary mixture of equal-sized hard spheres, the third virial coefficient obtained for the McGlashan equation reproduces the exact third coefficient.

1.5 CONCLUSION

The arguments in favour and against the two equations of state investigated are now clear. If the system of interest involves a binary mixture of hard spheres of equal sizes, the Mansoori and McGlashan equations are equivalent at all densities, and both provide a relatively accurate

representation of hard sphere properties. For binary mixtures with hard spheres of different sizes, the Mansoori equation is a better representation of the hard sphere properties than the McGlashan equation, and the superiority of ^{the} Mansoori expression is greatest when the difference in size is large. Therefore, the Mansoori et al. equation will be better suited to investigate the phase equilibria of solutions of large spherical particles than the "one-fluid" expression of McGlashan et al.

In the next chapter the properties of binary hard sphere mixtures calculated using the Mansoori equation of state are compared with the exact results of computer simulations. A special emphasis is placed on mixtures with large size differences to check the Mansoori equation's reliability under these extreme conditions.

CHAPTER 2

COMPUTER SIMULATIONS OF HARD SPHERE MIXTURES

Only a few problems in statistical mechanics are exactly soluble, and these include systems such as the ideal monatomic gas, the Einstein crystal, and the two-dimensional Ising model. In cases where an exact solution is not possible, or is intractable, a straight-forward approximation may enable a reasonable analysis of the problem to be made. The evaluation of the virial expansion for dilute, imperfect, gases is a good example of the use of such an approximate scheme. However, many approximate theories fail when applied to liquids.

Computer simulations play a very important role in enabling us to obtain essentially exact results for systems in statistical mechanics where exact solutions are not possible and only approximate methods are available. Hence, a valuable use of computer simulations is to test these approximate schemes, discriminating between the good and bad theories. Furthermore, computer generated results verify the fundamental validity of the underlying conceptual model when compared with the results of real experiments by providing a direct route from the microscopic details of the

system to the macroscopic properties of experimental interest.

In this chapter binary mixtures of hard spheres of different sizes and compositions with diameter ratios ranging from $d_1/d_2=3/5$ to $d_1/d_2=1/20$ and for mole fractions between $x_2=0$ and $x_2=1$ are investigated using computer simulations. The results are compared with those calculated from the equation of state for hard sphere mixtures proposed by Mansoori et al. (see Chapter 1). Although some computer-generated data are already available for mixtures of hard spheres, only a few size ratios and compositions have been examined (see Section 2.4) so that a complete and thorough testing of the Mansoori equation is not possible until further simulations are undertaken at other size ratios and mole fractions. Furthermore, since the Mansoori equation of state is used in future chapters to calculate the phase equilibria and critical points of hard core mixtures with large size differences ($d_1/d_2=1/20$ and $d_1/d_2=0$), it was necessary to check that the equation accurately reproduces the hard spheres properties, even at these extreme size ratios.

The random "spinning-of-the-wheel" Monte Carlo MC technique is used to obtain ensemble averages for mixtures of hard spheres in the canonical NVT ensemble with the standard canonical Monte Carlo MC(NVT) method, as well as in the isothermal-isobaric NPT ensemble with constant-pressure Monte Carlo MC(NPT). Molecular dynamics MD simulations of hard sphere mixtures are also undertaken which enable a

comparison with the Mansoori and Monte Carlo results, and provide dynamical information for the systems of colliding spheres. In the following sections these methods of computer simulation are described briefly, after which the computer-generated results for hard sphere mixtures are presented. There are more detailed descriptions of the techniques in standard text books [15],[16],[17].

2.1 MONTE CARLO SIMULATIONS

The Monte Carlo method was proposed independently by Mayer and by von Neumann and Ulam [18]. Mayer suggested that the method was useful in statistical mechanical calculations of liquids, while Ulam proposed it as a procedure of general usefulness.

The Monte Carlo technique deals with multi-dimensional integrals by integrating over a random sampling of points instead of over a regular array of points. In practice, however, this method is not useful for high density states of configurational energy U because configurations with very low weighting, where $\exp(-U/kT)$ is very small, are chosen with high probability, due to molecular overlaps. To overcome this problem Metropolis et al. [19] employed a modified Monte Carlo scheme where instead of choosing configurations randomly and then weighting them with $\exp(-U/kT)$, they choose configurations with a probability $\exp(-U/kT)$ and weight them evenly. This method is what is now usually referred to as the Monte Carlo method.

The original simulations were for systems of hard spheres and disks in the canonical NVT ensemble. However, within a few years, Monte Carlo simulations were performed for Lennard-Jones molecules by Wood and Parker [20] which allowed the computer-generated data to be compared with the experimental data of, for example, liquid argon. The technique of Monte Carlo simulations in the canonical ensemble MC(NVT) is described in the following section.

2.1.1 Canonical NVT Ensemble

The object of the Monte Carlo method in the canonical ensemble is to evaluate expectation values of a function $f(r^N)$ which depends on the coordinates of the N particles for a thermodynamic system of volume V in equilibrium at temperature T . Strictly speaking we have to take the thermodynamic limit with both the number of particles and volume tending to infinity. The canonical ensemble average of f is then given by

$$\langle f \rangle_{NVT} = \frac{\int_V dr^N f(r^N) \exp(-U(r^N)/kT)}{\int_V dr^N \exp(-U(r^N)/kT)}$$

where $U(r^N)$ is the configurational potential. In the simplest case the average of the configurational potential is obtained when f is U itself. The multiplicity of the integral is of the order of 10^{23} for macroscopic systems and its evaluation by brute-force methods is extremely difficult even for systems of a few hundred particles. The

conventional Monte Carlo brute-force method of Ulam [18] for evaluating this integral is to choose points at random in all of phase space to produce a number M of different configurations, labelled i from 1 to M . In other words we get a sum of terms

$$\langle f \rangle_{NVT} = \frac{\sum_{i=1}^M f(i) \exp(-U(i)/kT)}{\sum_{i=1}^M \exp(-U(i)/kT)}$$

However, as stated previously, this is very inefficient except at very low densities because virtually all choices of i will result in large values of $U(i)/kT$ since we are quite likely to have two particles "overlap". Such states give rise to virtually no contribution to the sum. A solution to this problem would be to choose configurations for which $\exp(-U(i)/kT)$ is large, but this type of biased Monte Carlo procedure is extremely difficult.

On the other hand if configuration, i , is chosen with the probability , $\exp(-U(i)/kT)$, then the ensemble average is simply

$$\langle f \rangle_{NVT} = \frac{\sum_{i=1}^M f(i)}{M}$$

The introduction of this Metropolis importance sampling scheme solves the problem. The next question which arises is how to sample according to this probability distribution.

There is no unique way of doing this, but a recipe which is commonly used is the following. An initial

configuration, i , is chosen and a particle of the system is selected either cyclically or at random. The selected particle is then moved along each axis by random amounts in the interval $-\beta$ to $+\beta$ to produce a new configuration, j . For molecular systems a random reorientation of the selected molecule is also undertaken. The difference in energy between the new and the old configuration is then evaluated:

$$\Delta U = U(j) - U(i)$$

This is a relatively fast calculation in terms of overall computing time because it only involves neighbours of the particle which moved. If the change in energy is negative with $U(j) < U(i)$ the move is accepted because j is a more probable configuration than i , and a bias toward configurations which contribute more significantly in the sum is desired. However, in order not to get trapped in one region of high probability, the move is not necessarily rejected if $U(j) > U(i)$. A move corresponding to an increase in energy is accepted with a probability $\exp[-(U(j)-U(i))/kT]$ by comparing the probability with a number randomly distributed between 0 and 1. If the value of $\exp[-(U(j)-U(i))/kT]$ is greater than the random number, the new configuration is accepted. For values of $\exp[-(U(j)-U(i))/kT]$ which are less than the random number, the move is rejected and the system is returned to the initial configuration which is recounted in the sum. Metropolis et al. [19] and Wood and Parker [20] have shown

in the language of Markov processes that this procedure produces a canonical distribution.

By starting with an initial configuration such as a face-centred cubic lattice, and by randomly moving the particles as described above, equilibrium is achieved. Some tens of thousands of moves may be required depending on the system being investigated. Because only a finite system can be studied, periodic boundary conditions with the usual minimum image distance interaction are used. This confines the finite number of molecules to a unit cubic space, representing in effect an infinite three-dimensional space made up of unit translations of the basic cell. The value of β representing the displacement of each particle is arbitrary, but is usually chosen to give a success rate for the moves of the order of 50%. This means that we are sampling regions of phase space with high probability configurations for a sufficient amount of "time". Typically β is about 1/20 of the particle diameter. Once in equilibrium the ensemble averages are accumulated so that the sum of the function $f(r^N)$ under investigation is determined for a number of configurations. Good statistics for the average value of $f(r^N)$ are obtained with a large enough number of moves M . Clearly, this enables any point in configurational space to be reached so that method is ergodic.

This general Monte Carlo scheme is simple in the case of systems of hard spheres. A particle is chosen and moved at random, and the sphere's new position is then checked for

any overlaps with all the other spheres. All trial moves involving an overlap are immediately rejected since $\exp-\{(U(j)-U(i))/kT\}=0$ would be smaller than any random number between 0 and 1. Equally, all moves which do not involve overlaps are immediately accepted. As before in the case of a rejection the old configuration is recounted in the average.

The system of particular interest is a binary mixture of N hard spheres with N_1 spheres of size d_1 and N_2 spheres of size d_2 in a given volume V . The initial configuration for the system is generated by randomly distributing the large and small molecules on a simple face-centred cubic lattice. However, this limits the approach to a certain density range because overlaps occur at higher densities. The problem can be overcome by swelling the sphere diameters throughout the simulation to higher density states without overlaps, using various scaling techniques [21],[22]. This procedure generates high density configurations which can be used as starting points in the Monte Carlo simulations. An alternative and more effective way of obtaining these higher density configurations involves using isothermal-isobaric NPT Monte Carlo simulations which will be described in Section 2.1.2.

Once the initial configuration of the hard sphere mixture is available at the required density the NVT Monte Carlo simulation can be undertaken. A particle of either species 1 or 2 is chosen at random. In Smith and Lea's original simulations of hard sphere mixtures [23], the

spheres of both species are moved a random amount in the range $-\beta$ to $+\beta$ along each coordinate axis. However, when the two particles are very different in size, the smaller sphere can be moved a greater distance than the larger sphere without causing overlaps especially at higher densities. Hence, if both species are moved in the same random range, moves of the small spheres with a reasonable acceptance value will most certainly cause overlapping configurations for equivalent moves of the large spheres. This problem may result in an inefficient sampling of phase space, and it can easily be overcome by moving each species different random amounts. If a sphere of type 1 is chosen then it is moved a random distance in the range $-\beta_1$ to $+\beta_1$ along each axis, and similarly if a sphere of type 2 is chosen it is moved another random amount in the range $-\beta_2$ to $+\beta_2$. When the sphere is moved, its new position is checked for any overlaps. The move is rejected if an overlap occurs and accepted if no overlaps are found, and the ensemble averages are accumulated. As before β_1 and β_2 are chosen to give an acceptance rate of the order of 50%.

The radial distribution function for each pair interaction can be determined from the Monte Carlo simulation run. In turn, the thermodynamic properties of the system of hard spheres can be calculated from a knowledge of the radial distribution functions. After identifying the molecules of each species using reference numbers based on their initial coordinates, the configurations obtained during the course of the simulation

are analysed by counting the number of each of the 1-1, 1-2, and 2-2 molecular pairs whose molecular separations lie in a series of equal intervals. In practice, this process requires quite a lot of computer time so that the configurations are analysed in this way only about every $N/2$ moves. The cumulative totals over many configurations computed separately for each type of pair interaction are recorded, and after suitable normalization give the pair distribution functions, g_{11} , g_{12} and g_{22} .

The thermodynamic properties of hard sphere molecules depend only on the distribution functions evaluated at the point of contact, obtained by short extrapolations of the pair distributions. A common extrapolation involves fitting the best straight line through the data of $\ln(g(r))$ against r using a least squares procedure to give the contact value of $g(d)$ at a separation of d . For a binary mixture of hard spheres, the equation of state can be written

$$Z = \frac{PV}{NkT} = 1 + \frac{2\pi N}{3V} (x_1^2 d_1^3 g_{11}(d_1) + 2x_1 x_2 d_{12}^3 g_{12}(d_{12}) + x_2^2 d_2^3 g_{22}(d_2))$$

where N is the total number of molecules, and x_1 and x_2 are the mole fractions of species 1 and 2 respectively. $g_{11}(d_1)$ is the pair distribution function for 1-1 interactions in the mixture evaluated at contact $r=d_1$, $g_{12}(d_{12})$ is the contact value for the 1-2 pairs evaluated at $r=(d_1+d_2)/2=d_{12}$, and $g_{22}(d_2)$ is the contact value for the 2-2 pairs at $r=d_2$. Hence, by determining the contact values

of the pair distribution functions, a canonical NVT Monte Carlo simulation provides a means of obtaining the equation of state for a mixture of hard spheres.

It must be noted that by carefully choosing the configurational weighting probability corresponding to a particular ensemble, the Monte Carlo method can be generalized for ensembles other than the canonical ensemble. In the next section the isothermal-isobaric NPT Monte Carlo technique is described.

2.1.2 Isothermal-Isobaric NPT Ensemble

In NVT Monte Carlo simulations of hard sphere mixtures, the equation of state must be calculated from the values of the radial distribution functions at contact which can only be estimated by extrapolation. The limited precision of the resulting estimate introduces a further error into the calculated result. This difficulty can be overcome by turning to isothermal-isobaric Monte Carlo MC(NPT) simulations, since the calculation of the equation of state is more direct in the NPT ensemble. The first constant-pressure Monte Carlo simulations were performed by Wood for systems of hard disks and spheres [16],[24],[25], and the technique was extended by McDonald to cover continuous potentials for mixtures of Lennard-Jones molecules [26],[27].

The isothermal-isobaric NPT ensemble average of a function $f(r^N, V)$ which is a function of the coordinates and the volume is given by

$$\langle f \rangle_{\text{NPT}} = \frac{\int_0^\infty dV \exp(-PV/kT) \int_V dr^N f(r^N, V) \exp(-U(r^N, V)/kT)}{\int_0^\infty dV \exp(-PV/kT) \int_V dr^N \exp(-U(r^N, V)/kT)}$$

For computational reasons it is convenient to scale the coordinates with respect to the length of the simulation cube L with $S=r/L$ so that the integrals of r become integrals of S over the unit cube. The NPT ensemble average with an additional factor of V^N which comes from the volume element dr becomes

$$\langle f \rangle_{\text{NPT}} = \frac{\int_0^\infty dV \exp(-PV/kT) V^N \int_{\text{cube}} dS^N f(S^N, V) \exp(-U(S^N, V)/kT)}{\int_0^\infty dV \exp(-PV/kT) V^N \int_{\text{cube}} dS^N \exp(-U(S^N, V)/kT)}$$

The Metropolis Monte Carlo scheme for the NPT ensemble follows from the ideas discussed in Section 2.1.1 for the NVT ensemble so that states with a probability

$$\exp[-(PV + U(S^N, V))/kT + N \ln V]$$

are chosen. A new configuration j is generated from the initial configuration i at a given pressure and temperature by displacing a molecule randomly and making a random volume change. As with the canonical Monte Carlo method the particle is moved randomly in the range $-\beta$ to $+\beta$ along each

axis. Random changes in volume are achieved by varying the box length L with random distributions chosen between $-\beta_L$ and $+\beta_L$. As before the choices of values for β and β_L are arbitrary and are adjusted by trial and error to give an acceptance rate of about 50%. To determine whether the new configuration is accepted or rejected the following quantity is calculated

$$\Delta H = [U(j) - U(i)] + P[V(j) - V(i)] - NkT \ln[V(j)/V(i)]$$

and the value of this function is closely related to the enthalpy change in moving from state i to j . The move is accepted with a probability equal to $\exp(-\Delta H/kT)$ by a comparison with a random number between 0 and 1. A move may proceed with a change in particle position, or a change in volume or a combination of both. In practice a change in volume is computationally more expensive than a change in particle position. Consequently, in a typical simulation the volume is changed after about every N particle moves, where N is the total number of particles.

The constant-pressure Monte Carlo simulation is started from an initial configuration and run with periodic boundary conditions until equilibrium is achieved and the volume oscillates around a mean value corresponding to the pressure. Further configurations are then undertaken to accumulate the averages.

This general procedure is even simpler for hard sphere systems. In the case of binary mixtures of hard spheres, it is useful to reduce the volume and pressure with respect to the diameter of the smaller sphere, d_1 , such that $P_r = P d_1^3 / kT$ and $V_r = V / d_1^3$. The NPT ensemble average then becomes

$$\langle f \rangle_{NPT} = \frac{\int_0^\infty dV_r \exp(-P_r V_r) V_r^N \int_{\text{cube}} dS^N f(S^N, V_r) \exp(-U(S^N, V_r) / kT)}{\int_0^\infty dV_r \exp(-P_r V_r) V_r^N \int_{\text{cube}} dS^N \exp(-U(S^N, V_r) / kT)}$$

Actually, the simulations are carried out using variables scaled with respect to the box length, L , where $d = d_1 / L$, $V_r = 1 / d^3$ and $dV_r = -3 / d^4$. In this case $\langle f \rangle$ is given by

$$\langle f \rangle_{NPT} = \frac{\int_0^\infty d(d) \exp(-P_r d^{-3}) d^{-(3N+4)} \int_{\text{cube}} dS^N f(S^N, d) \exp(-U(S^N, d) / kT)}{\int_0^\infty d(d) \exp(-P_r d^{-3}) d^{-(3N+4)} \int_{\text{cube}} dS^N \exp(-U(S^N, d) / kT)}$$

The Monte Carlo method is then implemented by generating a Markov chain of states which has a limiting distribution proportional to

$$\exp[-P_r d^{-3} - U(S^N, d) / kT - (3N+4) \ln d]$$

When the system is changed from a state i to a state j , the change in the function H is calculated in the following way

$$\Delta H = [U(j) - U(i)] + P_r [d^{-3}(j) - d^{-3}(i)] kT + (3N+4) kT \ln[d(j) / d(i)]$$

The initial configuration is generated by randomly distributing the N different-sized spheres on a face-centred cubic lattice inside a cubic box with periodic boundary conditions. The system's pressure and temperature are fixed, and the initial volume and density of the system are chosen to produce a configuration without any overlaps. As with NVT Monte Carlo simulations, one of the particles is chosen at random and displaced a random distance in the range $-\beta_1$ to $+\beta_1$ for species 1, and $-\beta_2$ to $+\beta_2$ for species 2. The move is rejected if it causes an overlap and is accepted if no overlaps are obtained. After about N moves with the usual accumulation of averages, a volume change is undertaken by changing the box length L randomly between $-\beta_L$ and $+\beta_L$. If the volume change generates overlaps the change is rejected, but if no overlaps are caused the volume change is accepted with a probability $\exp(-\Delta H/kT)$. The accumulation of averages is implemented in the normal way after equilibration is achieved.

As with canonical NVT Monte Carlo simulations, the radial pair distribution functions can be obtained during the course of the run, and from estimates of their contact values, the hard sphere mixture's equation of state can be evaluated. However, with NPT Monte Carlo simulations the volume and hence the reduced density ξ of the hard sphere system is available directly from the average value of the volume accumulated during the course of the simulation. Consequently, the errors present in arriving at the equation of state using the canonical Monte Carlo method are

by-passed when we turn to the constant-pressure Monte Carlo method. Although the NPT Monte Carlo method seems superior to the NVT method because of this, it appears that the fluctuations of the averages calculated in a NPT simulation are greater than those associated with the averages in an NVT simulation. In the case of binary mixtures of hard spheres the errors involved are comparable for the two ensembles.

A distinct advantage of a constant-pressure Monte Carlo simulation over a canonical Monte Carlo simulation, and for that matter a molecular dynamics simulation, is the ease with which it can generate configurations of high density. Theoretically, any density up to hard sphere close-packing can be achieved by adjusting the pressure to high enough values, but practically this can be quite a slow process. Reduced densities of the order of $\xi=0.6$ can easily be attained for binary mixtures of hard spheres varying substantially in size after a reasonable number of configurations, such as 500 000. Configurations at these high densities are difficult to achieve using conventional NVT Monte Carlo and molecular dynamics techniques, although tedious scaling procedures have been used [21],[22]. The high density configurations obtained from the isothermal-isobaric Monte Carlo simulations can easily be used as initial configurations in subsequent molecular dynamics simulations.

2.2 MOLECULAR DYNAMICS SIMULATIONS

The first molecular dynamics simulations were performed by Alder and Wainwright for a hard sphere system [28]. The molecular dynamics method they describe is specifically for simulations involving particles with discontinuous potentials such as hard spheres and square wells [29]. Rahman was the first to describe the application of molecular dynamics to systems with continuous potentials such as Lennard-Jones molecules [30].

In a molecular dynamics simulation, a system of N particles is distributed within a cell of volume V . The cell is usually cubic in shape, and because the size of the system which can be studied economically is extremely small, periodic boundary conditions identical to those used in Monte Carlo simulations are imposed on the system. The particles are then assigned velocities selected in such a way as to make the total momentum zero. A Gaussian distribution for the velocities is usually chosen although this is not necessary. The trajectories of the particles are calculated by solving the classical equations of motion for a system of N molecules. For systems with discontinuous potentials, the motion of a particle is determined by the fact that its velocity changes suddenly whenever the distance between it and another particle becomes equal to the discontinuity in the potential. The account given in the following section is for a binary mixture of hard spheres of equal mass, m , but a generalization to other

discontinuous potentials and masses is straight-forward.

The first aim of molecular dynamics simulations of hard sphere mixtures is to locate the future collision times with force-free motion occurring between collisions. This requires the solution of a quadratic equation representing the collision time between two particles i and j . In a binary mixture of hard spheres of diameters d_1 and d_2 , the colliding particles can either be of the same species or of different species. At a time t the position and velocity of particle i are r_i and v_i respectively, and the position and velocity of particle j are r_j and v_j . These two particles will collide at a time $t+t_{ij}$ when

$$|r_{ij}(t+t_{ij})| = |r_{ij} + v_{ij}t_{ij}| = d_{ij}$$

where $r_{ij}=r_i-r_j$, $v_{ij}=v_i-v_j$. $d_{ij}=d_1$ if the colliding particles i and j are of species 1, $d_{ij}=d_2$ if i and j are of species 2, and $d_{ij}=d_{12}=(d_1+d_2)/2$ if i and j are particles of different species. If the above equation is squared then the expression becomes

$$v_{ij}^2 t_{ij}^2 + 2b_{ij}t_{ij} + r_{ij}^2 - d_{ij}^2 = 0$$

with $b_{ij}=r_{ij}v_{ij}$. By solving this quadratic equation for t_{ij} subject to the periodic boundary conditions of the box, the collision time between particles i and j is obtained as

$$t_{ij} = -(b_{ij} + (b_{ij}^2 - v_{ij}^2 (r_{ij}^2 - d_{ij}^2))^{1/2}) / v_{ij}^2$$

When b_{ij} is positive the two molecules are going away from each other and no collision occurs. Similarly, in cases where complex roots are obtained the particles will not collide. It must be noted that the smaller of the two roots obtained by solving the quadratic equation represents impact, whilst the larger root represents the second contact which would occur if the spheres were penetrable.

At the start of the simulation, a list of collision times is drawn up together with a list of which particles will be involved in the collisions. The smallest time $t(\min)$ in the list which represents the first collision is then determined, and all the particles are advanced by $t(\min)$.

The second part of the molecular dynamics simulation involves a computation of the collision dynamics in order to determine the velocities of the colliding pair after the collision has taken place. The velocity change after a collision follows from the conservation of energy and linear momentum, and from the requirement that the impulse acts along the line of centres. The velocities after a collision are

$$v_i(\text{after}) = v_i(\text{before}) + \delta v_i$$

$$v_j(\text{after}) = v_j(\text{before}) + \delta v_j = v_j(\text{before}) - \delta v_i$$

with the velocity change given by

$$\delta v_i = -(b_{ij}/d_{ij}^2)_{\text{contact}} r_{ij} = -\delta v_j$$

By evaluating b_{ij} at the moment of impact, the velocity change of the colliding pair is calculated and their new velocities are obtained, with the velocities of all the other particles remaining unaltered. The list of collision times is then updated for particles other than the colliding pair by subtracting $t(\min)$ from the previously stored collision times. In the case of collisions involving either of the colliding particles, the new collision times have to be recalculated. The new value of $t(\min)$ for the next collision is then located and the procedure is repeated. Together with the list of collision times and the corresponding list of colliding pairs, the other data which is stored during the simulation are the instantaneous values of the coordinates and velocities for all the particles.

The fact that the kinetic energy is conserved during the course of molecular dynamics simulations implies that the ensemble of interest is the microcanonical NVE ensemble with the number of particles, the volume and the energy of the system all constant. This implies that the temperature remains constant with $kT = m\langle v^2 \rangle / 3$ where $\langle v^2 \rangle$ is the mean-square velocity. A monitoring of the temperature during the simulation provides a means of checking the coding.

In a usual molecular dynamics simulation an equilibration run is performed to allow the velocities of the particles to equilibrate. After equilibration the values of the quantities of interest are accumulated for a further number of collisions until good statistics are

obtained. The average values of these quantities are then determined at the end of the run.

The average value of the pressure can be calculated in a molecular dynamics simulation by using the virial theorem

$$\frac{PV}{NkT} - 1 = \frac{1}{Nm \langle v^2 \rangle} \left\langle \sum_{i=1}^N r_i F_i \right\rangle$$

where F_i is the total force acting on particle i . In the case of hard spheres the force between particles acts only when a collision occurs so that the sum becomes a sum over the number of collisions occurring in the time T_{total} .

$$\frac{PV}{NkT} - 1 = \frac{\sum (r_{ij} v_{ij})_{\text{contact}}}{N \langle v^2 \rangle T_{\text{total}}} = \frac{\sum (b_{ij})_{\text{contact}}}{N \langle v^2 \rangle T_{\text{total}}}$$

This equation provides an accurate means of calculating the hard sphere mixture's equation of state. As with Monte Carlo simulations the pressure can also be calculated from the values of the radial pair distribution functions at contact. The contact values are estimated by extrapolating the pair distribution functions accumulated during the course of the run. Apart from the fact that calculating the distribution functions can be relatively expensive in terms of overall computer time, the estimates of the contact values introduce an uncertainty which can be large at high densities. The direct route to the pressure via the virial theorem is a definite advantage of the molecular dynamics method over the canonical Monte Carlo method.

The transport properties of the system of hard spheres can also be examined during a molecular dynamics simulation. The diffusion coefficient is

$$D = \frac{1}{3} \int_0^{\infty} \langle v_i(t) \cdot v_i(0) \rangle dt$$

for a particle i with velocity v_i . For long enough times this equation reduces to the Einstein relation

$$D = \frac{1}{6t} \langle |r_i(t) - r_i(0)|^2 \rangle = \frac{\text{MSD}}{6t}$$

where MSD is the mean-square displacement of particle i at time t .

It is common to store particle trajectories which have not been subjected to periodic boundary conditions, but which represent the actual movement of the molecules in space. These trajectories are particularly useful in calculating the self-diffusion coefficient.

In the case of binary mixtures of hard spheres, the square of the distance moved by each sphere of type 1 or type 2 in a certain time t is calculated without the use of periodic boundary conditions. To improve the statistical accuracy these averages are computed for each of the N particles in the simulation, added together for the two separate sets corresponding to species 1 and 2, and then divided by the number of particles of each species. The diffusion coefficients for the small and large spheres are then computed separately by plotting the appropriate values of the mean-square displacement against time. A least

squares procedure is used to fit the best straight line through the data for each species, and the slope of the line, $6D$, gives the diffusion coefficient, D . An inspection of the diffusion coefficients obtained in the molecular dynamics simulations will prove to be very useful in determining whether the hard sphere system is in a liquid or solid-like state.

An important advantage of the molecular dynamics method when compared with the Monte Carlo techniques is that the molecular dynamics simulations enable the dynamical properties of the system to be studied. Furthermore, since all the particles move simultaneously in a molecular dynamics run, a more efficient sampling of phase space is achieved than with Monte Carlo simulations which proceed by only one move at a time. The difference is especially noticable for high density states when the Monte Carlo technique explores phase space very slowly due to overlaps. This ergodic problem will be investigated in the case of binary hard sphere mixtures in the following sections of this chapter by comparing the results of molecular dynamics simulations with those obtained for the same high density systems using Monte Carlo.

As with the canonical NVT Monte Carlo method, when the spheres of the mixture are very different in size, it is difficult to obtain initial high density configurations for molecular dynamics simulations by randomly placing particles on a lattice. This is because overlaps will occur as the density is increased. The isothermal-isobaric NPT method

described in Section 2.1.2 overcomes this problem. By adjusting the pressure in an NPT Monte Carlo simulation to a value corresponding to a high density state, the initial low density configuration equilibrates during the course of the simulation to the appropriate high density configuration. The high density configurations of hard sphere mixtures obtained by the constant-pressure Monte Carlo method can then be used as the initial high density configurations for molecular dynamics simulations.

The use of the isothermal-isobaric NPT Monte Carlo method in parallel with the molecular dynamics method provides a very powerful technique to investigate the properties of mixtures of hard spheres. Before the results of Monte Carlo and molecular dynamics simulations for binary hard sphere mixtures are discussed, a brief survey of the data available for the pure hard sphere system is undertaken.

2.3 PURE HARD SPHERES

The first canonical NVT ensemble Monte Carlo simulations of a pure hard sphere system were performed by Rosenbluth and Rosenbluth on the Los Alamos MANIAC computer [31]. These results were later found to be in error by Wood and Jacobson [32] who repeated the NVT Monte Carlo simulations and found that at high enough densities, $\eta > 0.49$, there was a phase transition from a liquid to a solid. Alder and Wainwright's molecular dynamics simulations [28],[33] also showed this phase transition. It appears that the initial Rosenbluth results do not predict this behaviour because of the inadequate chain length used in the simulations.

Thorough NVT Monte Carlo hard sphere simulations by Hoover and Ree [34] confirmed the existence of a definite first order phase transition where the fluid and solid phases are in thermodynamic equilibrium. The structure of the pure hard sphere system changes dramatically when the density is increased beyond the transition point as clusters of molecules start solidifying into a close-packed face-centred cubic crystal lattice. The system's radial distribution function above the solid transition density shows the characteristic peaks associated with a face-centred cubic arrangement [35].

In Figure 2.1 the molecular dynamics MD results of Alder are compared with the empirical Carnahan-Starling CS equation of state for pure hard spheres, and with the Percus-Yevick compressibility PY_C and virial PY_V equations.

These equations are discussed in more detail in Section 1.2 of Chapter 1. It is clear that none of the equations of state show the transition to the solid phase which is predicted by the computer simulations at about $\eta=0.49$ and $Z=10.3$. It must be noted that a molecular theory for the freezing of hard spheres proposed by Haymet [36] also predicts a transition from a liquid to a face-centred cubic solid, in good agreement with computer simulations.

However, along the liquid branch of the curve, the Carnahan-Starling equation accurately describes the behaviour of the hard sphere system far better than either the Percus-Yevick compressibility or virial equations. Consequently, the Carnahan-Starling equation is a very convenient starting point in thermodynamic calculations of pure hard core systems as will be described in Chapter 3.

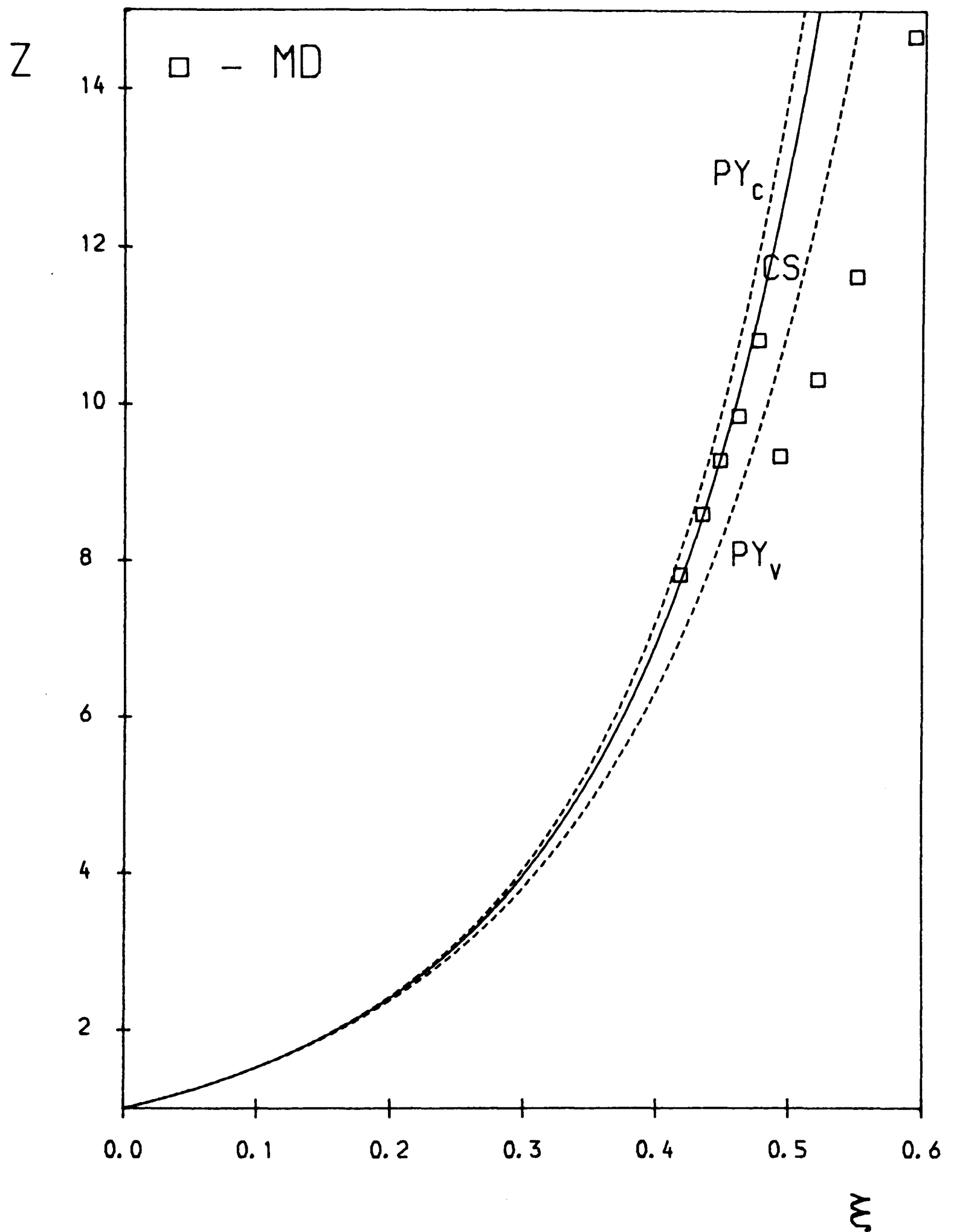


Fig. 2.1 The equation of state for pure hard spheres. The solid curve labelled CS represents the Carnahan-Starling equation, and the dashed curves PY_c and PY_v are the Precus-Yevick compressibility and virial equations. The squares represent the molecular dynamics results of Alder.

2.4 BINARY MIXTURES OF HARD SPHERES

Computer results for a few binary mixtures of hard spheres have already been reported in the literature. NVT Monte Carlo simulations of hard sphere mixtures were first performed by Smith and Lea [23] for an equimolar mixture $x_1=x_2=0.5$ with a diameter ratio of $d_2/d_1=5/3$, and Rotenberg [37] later carried out Monte Carlo simulations for equimolar mixtures with a diameter ratio $d_2/d_1=11/10$. Fries and Hansen [22] have undertaken NVT Monte Carlo simulations for hard sphere mixtures with $d_2/d_1=3/1$ and $d_2/d_1=2/1$ in the dilute regime of the larger spheres, i.e. $x_2<0.1$. The first molecular dynamics simulations of binary mixtures of hard spheres were reported by Alder [38] also for an equimolar mixture but this time for a size ratio of $d_2/d_1=3/1$.

The existing computer-generated results are in excellent agreement with the Mansoori et al. [11] equation of state for hard sphere mixtures described in Section 1.3 of Chapter 1. However, only a limited number of systems have been studied for a small range of diameter ratios and mole fractions. Because the Mansoori equation is used in subsequent parts of the research to calculate the thermodynamic properties of hard core mixtures with the diameter of one component much larger than the other, it is important to check the hard sphere equation for diameter ratios ranging from $d_2/d_1=1$ to about $d_2/d_1=20/1$ and for mole fractions in the range 0 to 1. Hence, a more systematic

study of binary hard sphere mixtures using isothermal-isobaric NPT Monte Carlo and molecular dynamics simulations is undertaken especially at high densities.

Broadly speaking it is true to say that bulk properties calculated by computer simulations are weakly dependent on the size of the system for $N > 100$ with the errors no larger than the inevitable statistical errors. Consequently, all the simulations reported in the following sections were for systems with a total of 108 particles in a cubic box.

For the constant-pressure NPT Monte Carlo simulations, the systems were initially equilibrated for between 500 000 and 1 500 000 configurations depending on the density. After equilibration the program was run for a further 1 500 000 to 2 000 000 configurations to accumulate the averages. A random change in volume was performed during the simulation for every 100 configurations. The computation of 500 000 configurations represented a computer time of about 2 hours on the VAX 11/785 at Oxford.

High density configurations were obtained using the NPT Monte Carlo technique and used to start off the molecular dynamics runs. After an equilibration of about 50 000 collisions for the molecular dynamics simulations, the averages were accumulated for between 150 000 and 300 000 collisions depending on the system. 150 000 collisions represented about 2 hours of VAX 11/785 time. Simulations involving the calculation of the radial pair distribution functions had to be run for longer times to achieve reasonable statistics.

2.4.1 The Equation Of State

In this section the results of the simulations are compared with the corresponding values calculated from the Mansoori equation shown as the solid curve in all the figures. The values of the compression factor $Z = PV/NkT$ for binary hard sphere mixtures with diameter ratios $d_2/d_1 = 5/3$, $3/1$, $5/1$ and $20/1$ are examined at various compositions x_2 and reduced densities ξ . Results are presented for mole fractions of $x_2 = 7/108 = 0.0648$, $11/108 = 0.1019$, $54/108 = 0.5$, and $97/108 = 0.8981$ with reduced densities up to about $\xi = 0.6$. High density states are primarily investigated because in this region the deviations of the Mansoori equation from the exact results are expected to be the greatest. The Monte Carlo statistical error in the compression factor Z was of the order 1-2%. Similarly, Z obtained from molecular dynamics simulations suffered from a statistical error of about 1-2% at moderate densities although for lower densities the error-bars were smaller.

2.4.1.1 System With $d_2/d_1 = 11/10$ -

The system with a size ratio $d_2/d_1 = 11/10$ was examined by Rotenberg [37]. As expected this mixture's properties do not depart significantly from the corresponding properties of the pure hard sphere system described in Section 2.3 because of the small difference in size between the two spheres. For liquid densities the computer results are in good agreement with the Mansoori equation, and as with the

pure rigid spheres, the liquid-solid phase transition appears at a reduced density of $\xi=0.49$. Systems with more significant size differences are investigated in more detail.

2.4.1.2 System With $d_2/d_1=5/3$ -

The results of isothermal-isobaric Monte Carlo MC(NPT) and molecular dynamics MD simulations for binary hard sphere mixtures with $d_2/d_1=5/3$ at various mole fractions are shown in Figs. 2.2-2.4. The solid curves in these figures are calculated using the Mansoori equation of state with the appropriate values of the size ratio and composition.

Fig. 2.2 displays the compression factor $Z=PV/NkT$ as a function of reduced density ξ for a dilute mole fraction of the larger spheres, i.e. $x_2=0.1019$. The Mansoori equation accurately predicts the exact Monte Carlo and molecular dynamics data shown as triangles and squares respectively for values of the reduced density below about $\xi=0.55$. However, the equation marginally underestimates the value of Z as the density is increased above 0.55, and hence the equation is expected to be a less accurate representation of the hard sphere system's properties at these higher densities. The solid transition is not observed at this mole fraction. The fact that the NPT Monte Carlo results are consistent with those obtained by molecular dynamics indicates that Monte Carlo phase space is sampled adequately, and there does not seem to be an ergodic problem even at high densities.

The results for the equimolar mixture $x_2=0.5$ with $d_2/d_1=5/3$ are depicted in Fig. 2.3. Smith and Lea's canonical Monte Carlo MC(NVT) data [23] shown as circles, and the constant-pressure Monte Carlo MC(NPT) and molecular dynamics MD results represented as triangles and squares respectively, are compared with the curve obtained from the Mansoori equation. The accuracy of the Monte Carlo results is comparable to that of the molecular dynamics data as well as being in good agreement with the Mansoori equation. The equation's ability to predict the hard sphere properties is maintained over the whole density range covered and no solid transition is observed.

When the mole fraction is increased to $x_2=0.8981$ a transition from a liquid to a solid-like phase is seen at higher densities. Fig. 2.4 summarizes the behaviour seen for the system $d_2/d_1=5/3$ with $x_2=0.8981$. The constant-pressure Monte Carlo MC(NPT) results and the molecular dynamics MD results follow the liquid branch of the Mansoori equation up to the solid transition at a reduced density of about $\xi=0.52$ and a compression factor of $Z=13.5$. Above the transition density the Mansoori equation overestimates the value of the compression factor while the exact results follow the solid branch of the curve. A systematic investigation of the solid transition for systems of different-sized spheres is undertaken in Section 2.4.2.

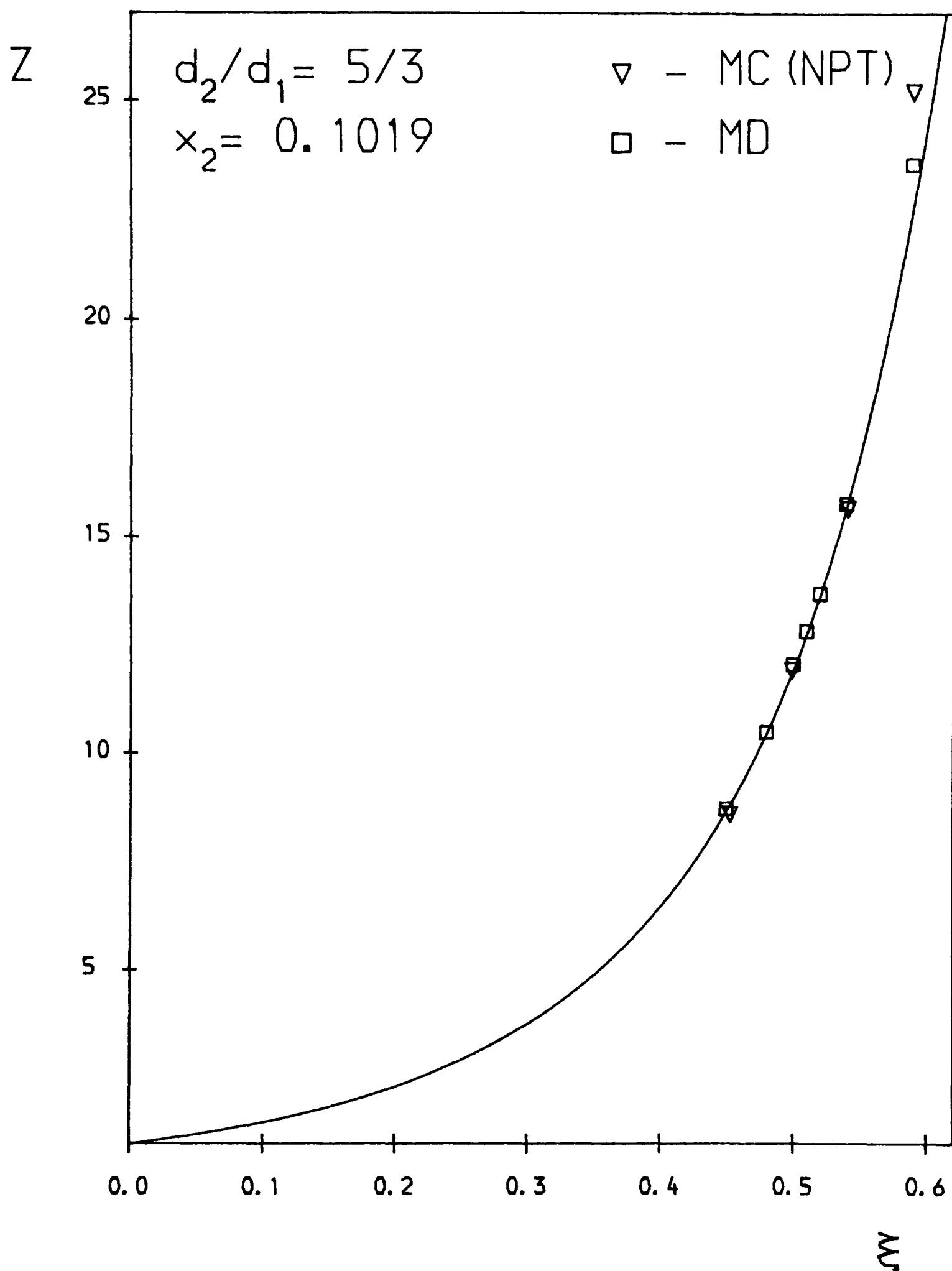


Fig. 2.2 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics data are represented by triangles and squares respectively, and the solid curve represents the Mansoori equation.

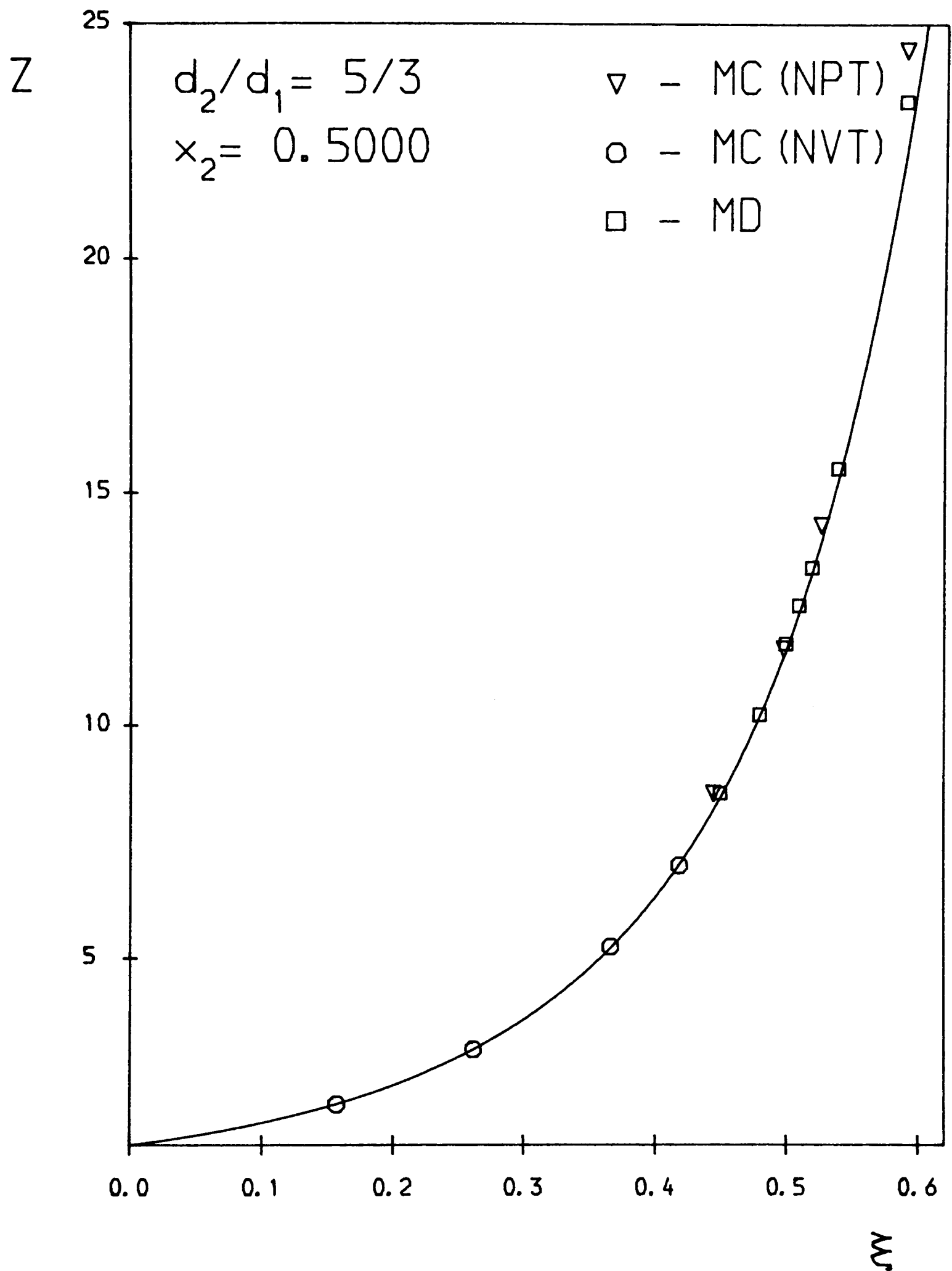


Fig. 2.3 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics data are represented by the triangles and squares respectively. The circles are the Monte Carlo results of Smith and Lea.

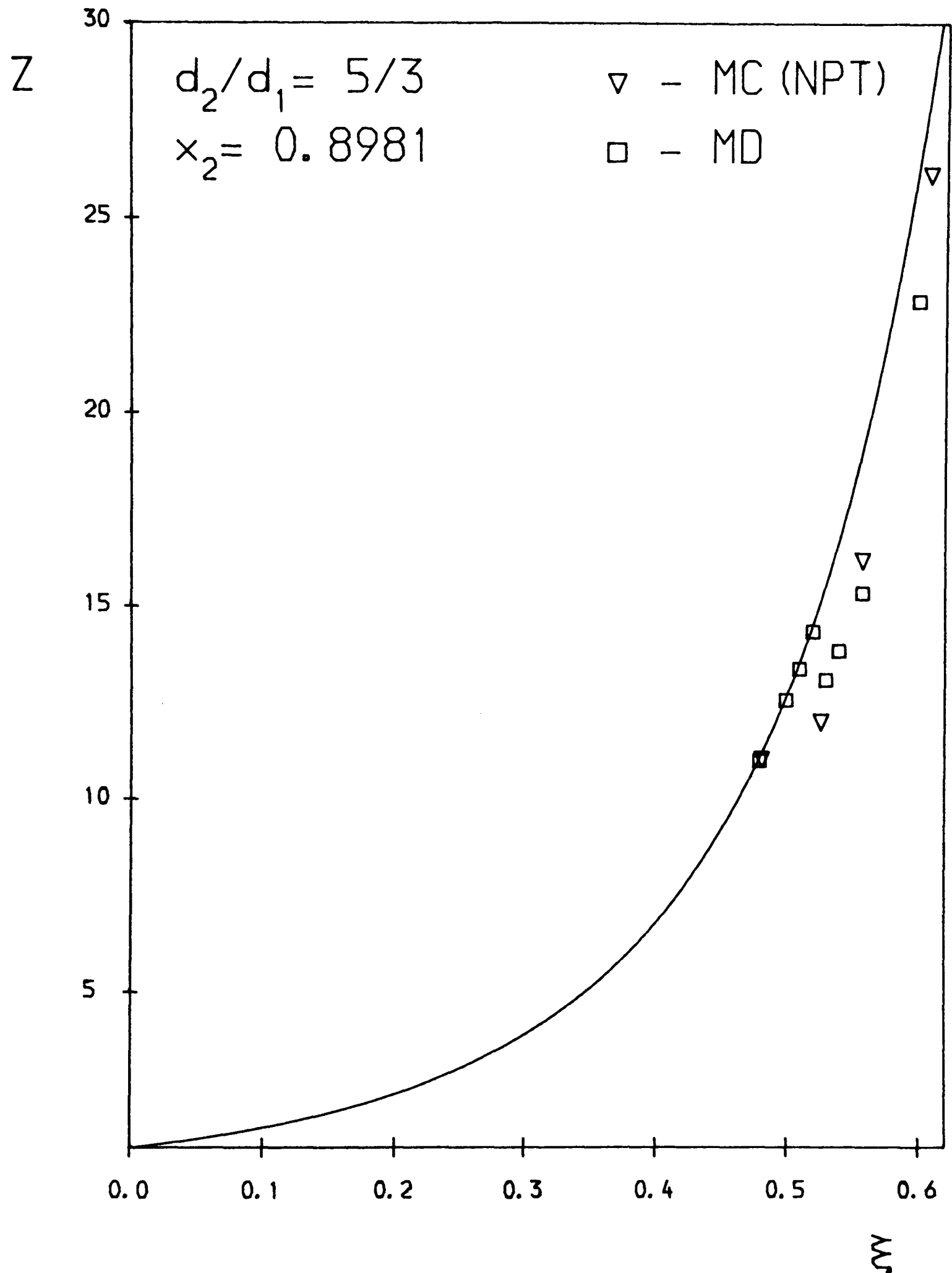


Fig. 2.4 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics data are the triangles and squares respectively, and the solid curve represents the Mansoori equation.

2.4.1.3 System With $d_2/d_1=3/1$ -

The canonical Monte Carlo MC(NVT) results of Fries and Hansen [22] and the molecular dynamics MD data of Alder [38] at mole fractions of $x_2=0.06$ and $x_2=0.5$ respectively are complemented with constant-pressure Monte Carlo MC(NPT) and further molecular dynamics calculations. It must be noted that for 108 particles the Fries composition of $x_2=0.06$ is not possible so that the next closest mole fraction of $x_2=0.0648$ was used.

The simulation data is compared with the Mansoori equation's results in Figs. 2.5-2.7. Fig. 2.5 represents a system with $d_2/d_1=3/1$ and $x_2=0.0648$. It is interesting to note that the NVT Monte Carlo data are consistent with the NPT Monte Carlo results. The computer and Mansoori results are in good agreement although a small deviation occurs at higher densities.

The system with $x_2=0.5$ is depicted in Fig. 2.6. Alder's molecular dynamics results are compared with isothermal-isobaric Monte Carlo MC(NPT) data, and also with the Mansoori equation. The agreement is good, within about 2%, even up to densities of the order of $\xi=0.6$.

Fig. 2.7 shows the results obtained for a composition of $x_2=0.8981$. Again the Mansoori results are seen to be consistent with the computer data along the liquid branch of the curve. At a density of about $\xi=0.53$ and a compression factor of $Z=14.2$ there is a transition from the liquid to the solid, and the Mansoori equation fails to predict this behaviour.

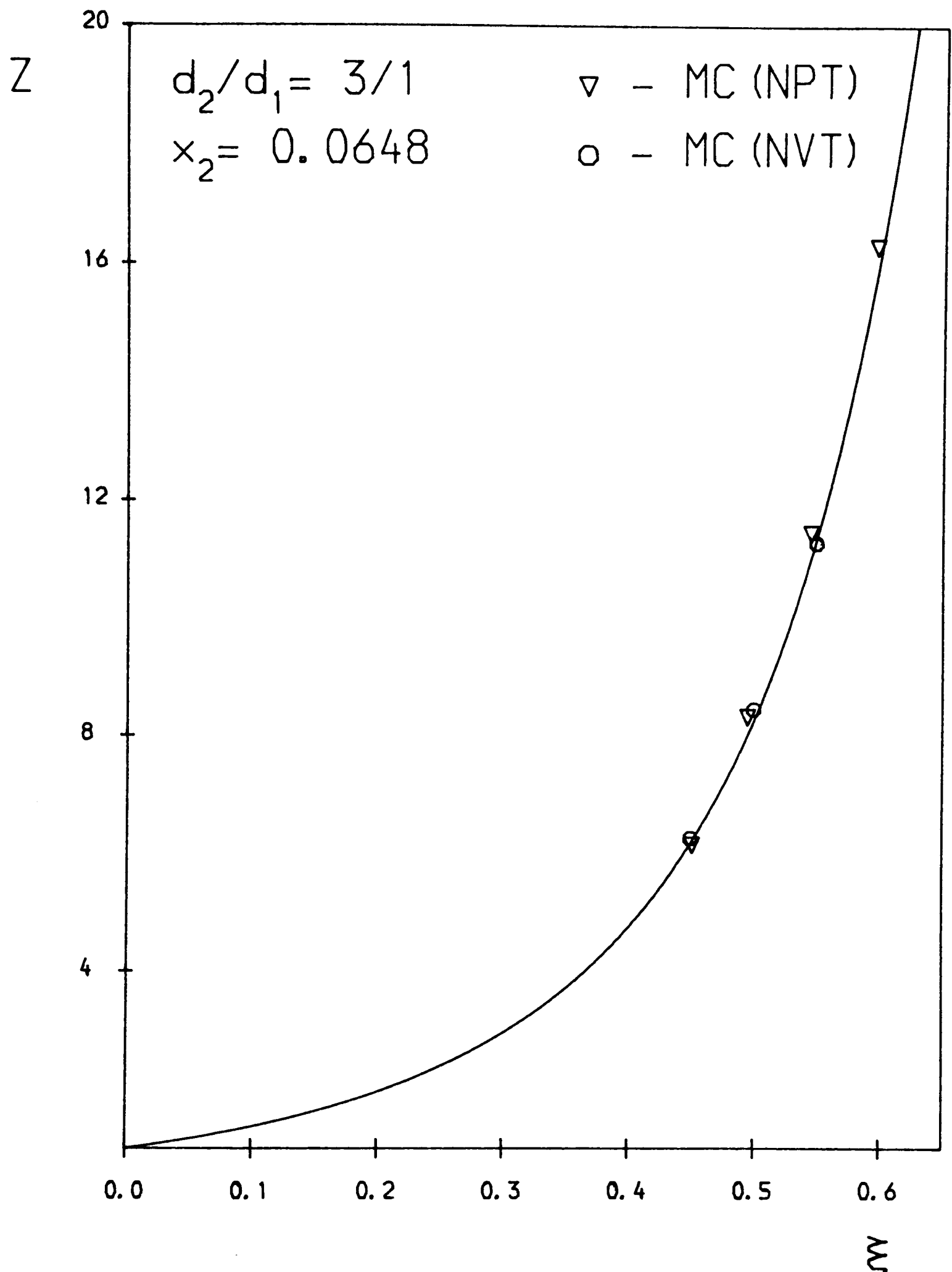


Fig. 2.5 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo data and the Fries NVT Monte Carlo results are represented by triangles and circles respectively, and the solid curve represents the Mansoori equation.

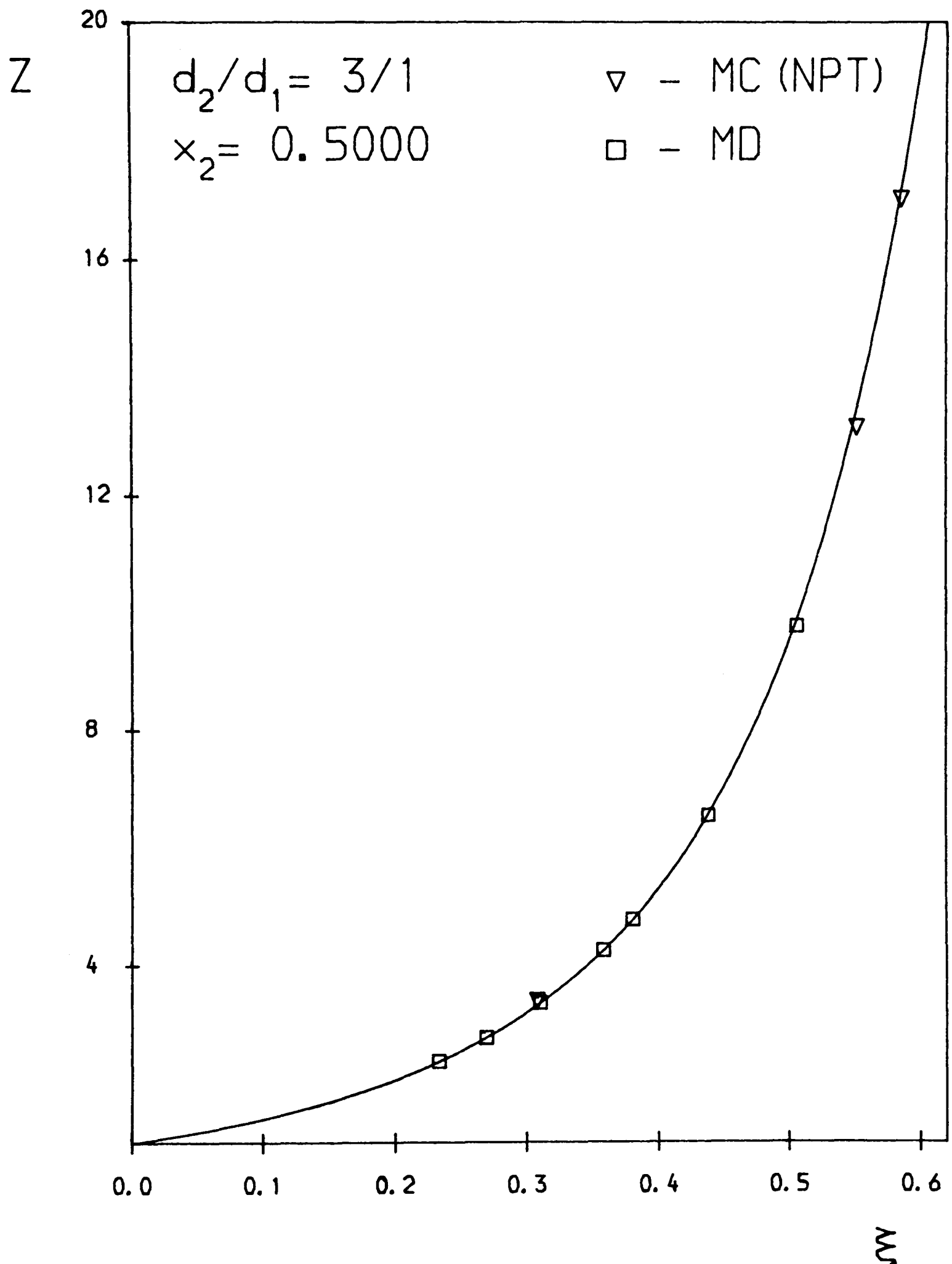


Fig. 2.6 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo data and Alder's molecular dynamics results are the triangles and squares respectively.

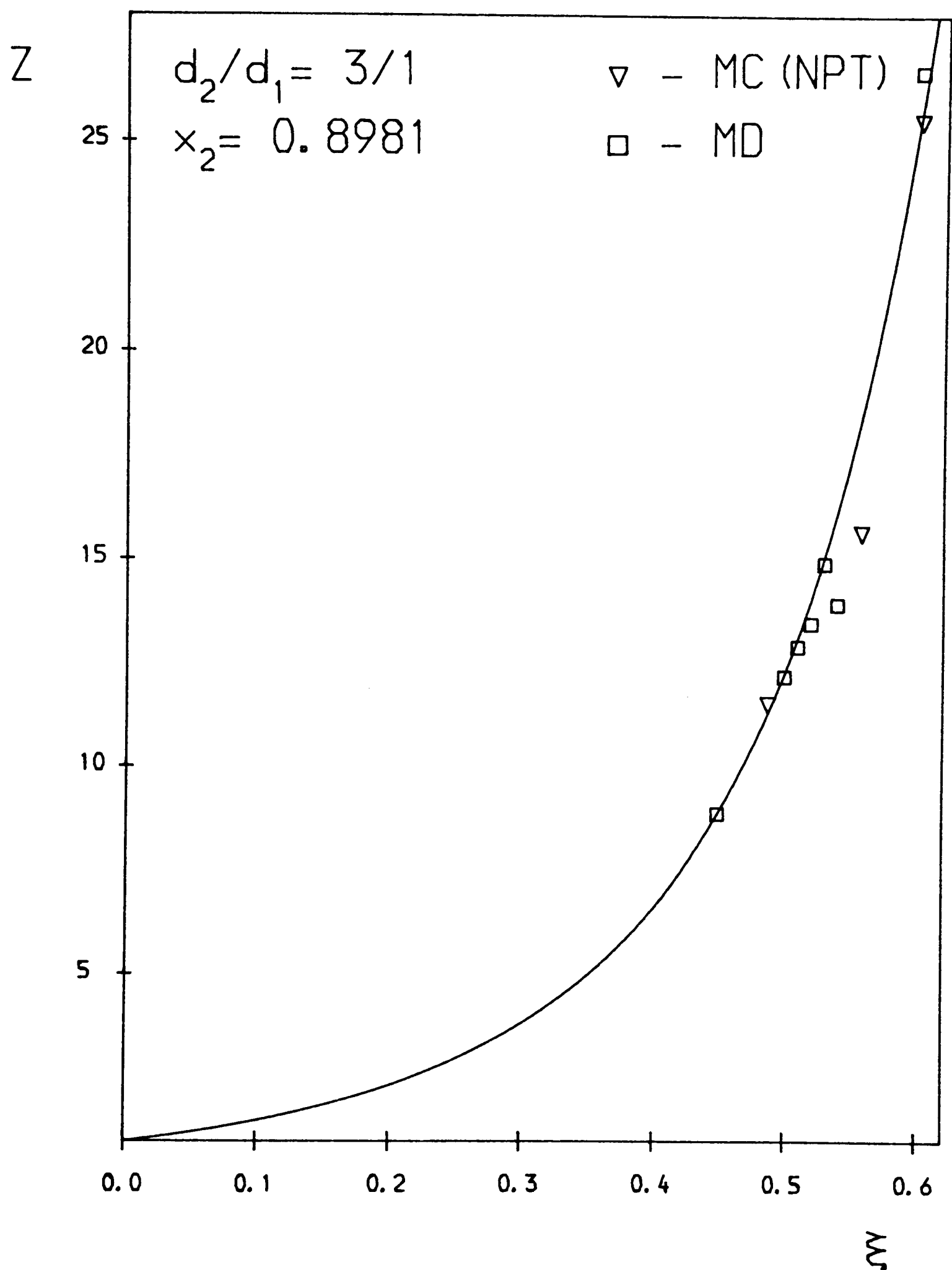


Fig. 2.7 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics data are the triangles and squares respectively, and the solid curve represents the Mansoori equation.

2.4.1.4 System With $d_2/d_1=5/1$ -

The equation of state of a binary mixture of hard spheres with a size ratio of $d_2/d_1=5/1$ is examined in Figs. 2.8-2.10. Fig. 2.8 for a mole fraction of $x_2=0.1019$ compares the results of molecular dynamics and constant-pressure NPT Monte Carlo simulations with the curve obtained using the Mansoori equation. At low densities the equation is in good agreement with the computer data, but negative deviations occur at densities above about $\xi=0.5$ when the Mansoori equation starts underestimating the exact values of Z .

A liquid-solid transition is seen for the equimolar composition of $x_2=0.5$ in Fig. 2.9. The hard sphere equation predicts the mixture's properties in the liquid regime, but fails at a solid transition density of about $\xi=0.52$ and a compression factor of $Z=9.0$. The equation overestimates the values of Z for densities along the solid branch of the curve.

The behaviour of the system with a composition $x_2=0.8981$ is very similar to that of the equimolar mixture with a good agreement between the Mansoori results and the computer data up to the solid transition density. This occurs at about $\xi=0.53$ and $Z=13.5$ as shown in Fig. 2.10.

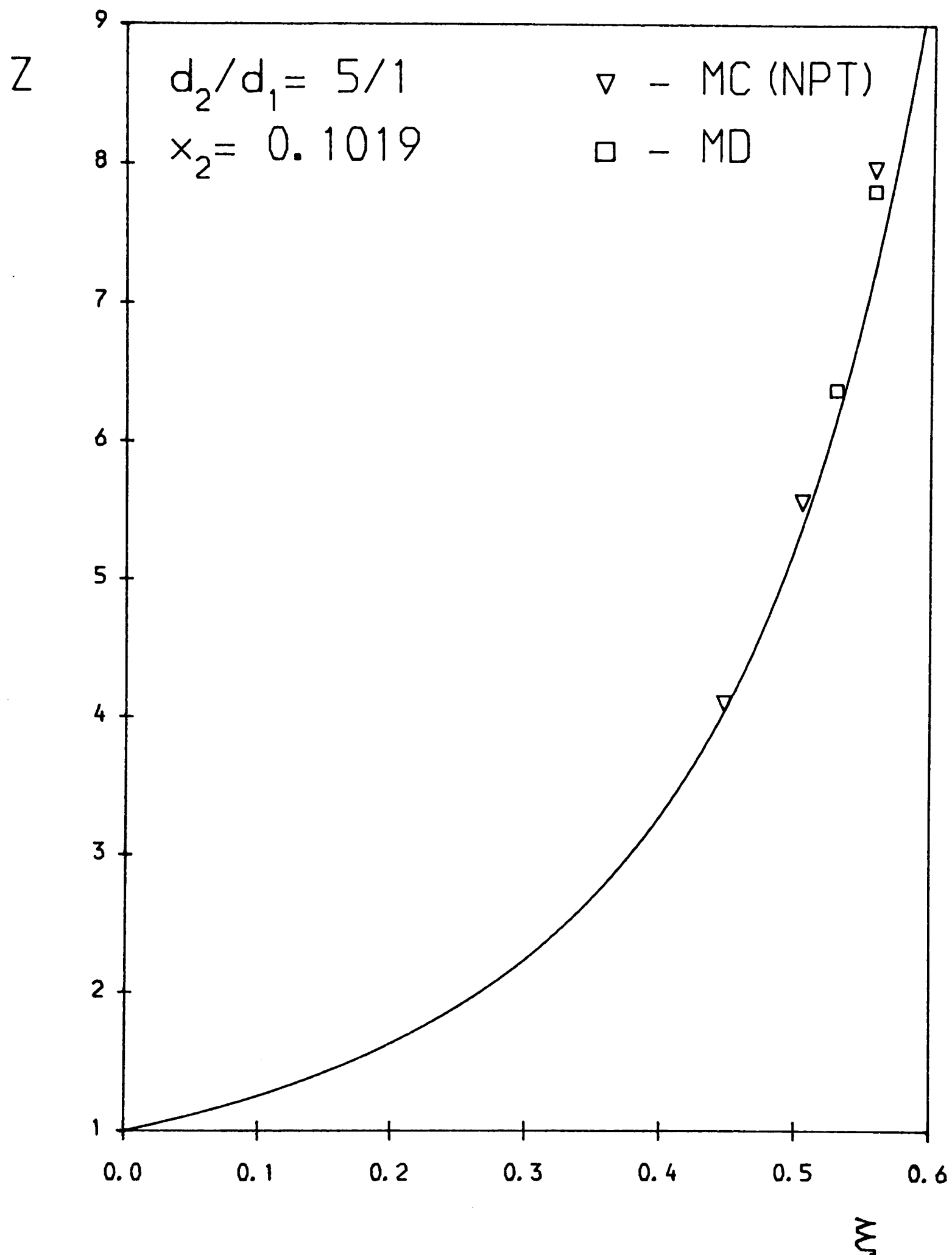


Fig. 2.8 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics results are represented by triangles and squares respectively, and the solid curve represents the Mansoori equation.

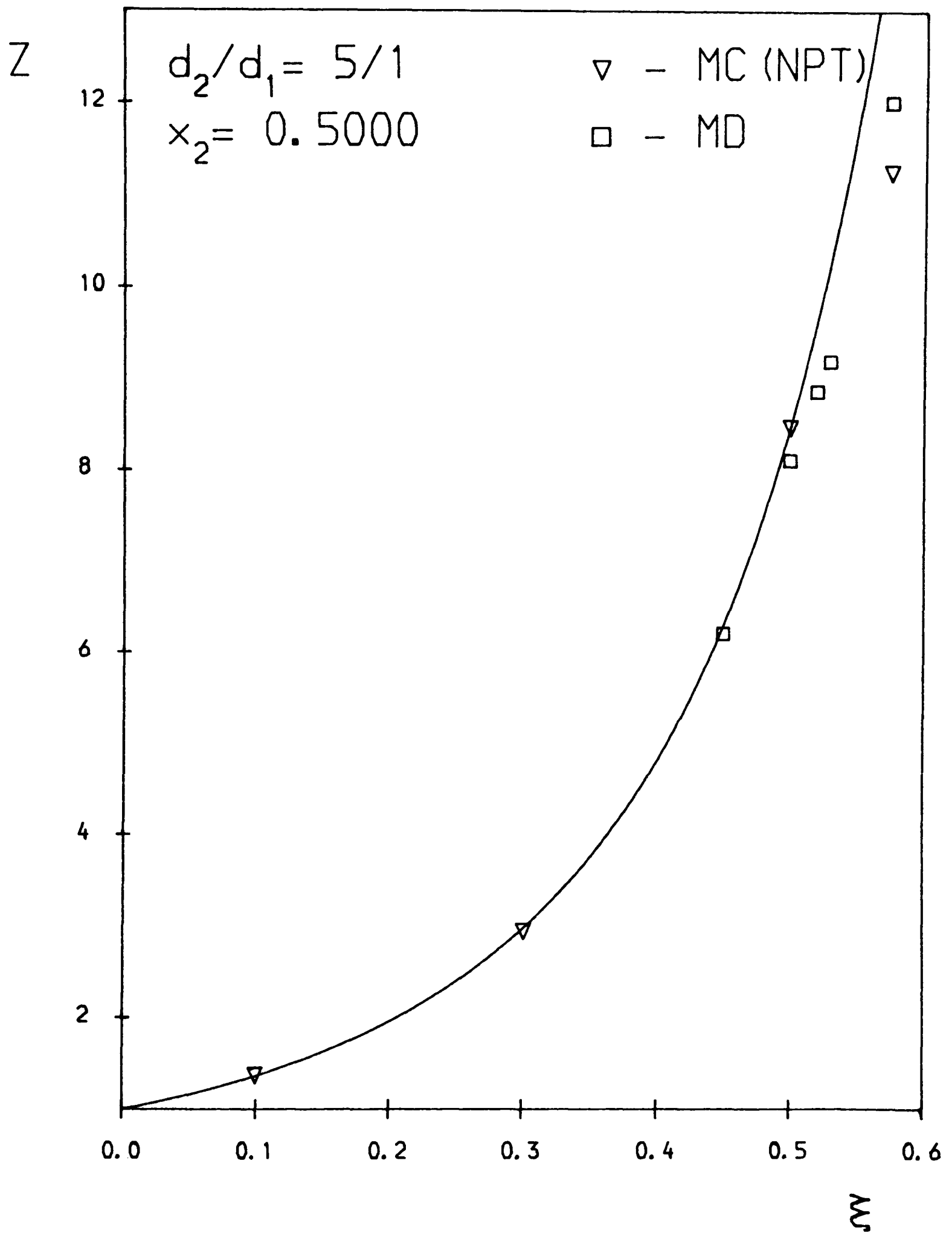


Fig. 2.9 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics results are the triangles and squares respectively.

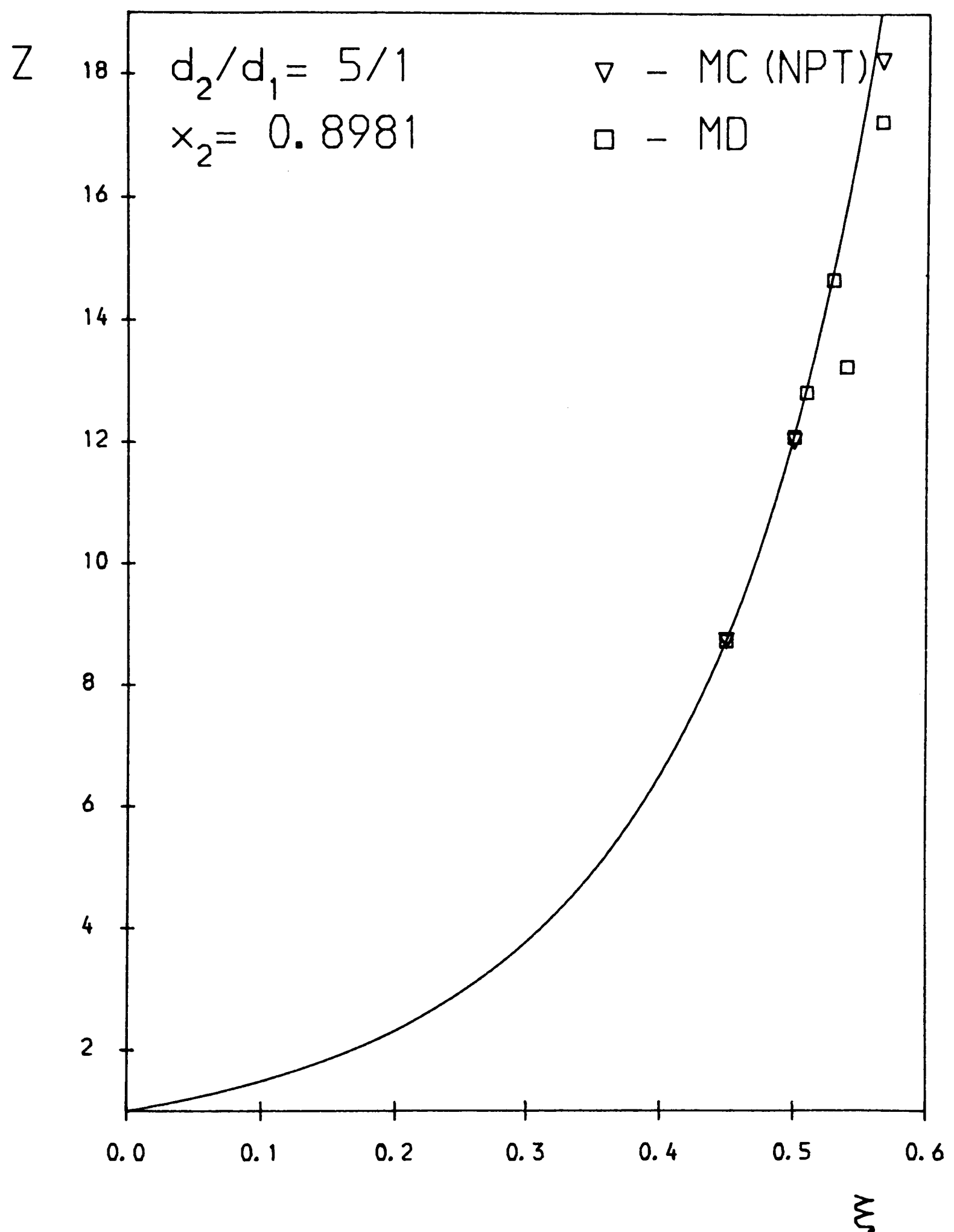


Fig. 2.10 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics data are the triangles and squares respectively, and the solid curve represents the Mansoori equation.

2.4.1.5 System With $d_2/d_1=20/1$ -

The final system investigated was the mixture with a diameter ratio of $d_2/d_1=20/1$ shown in Figs. 2.11-2.13. Fig. 2.11 is for a mole fraction of $x_2=0.1019$ from which it is clear that the Mansoori equation is a good representation of the hard sphere properties up to a density of about $\xi=0.5$ after which it starts to underestimate the compression factor quite markedly. This is consistent with the molecular dynamics contact values obtained for the radial distribution functions which are all higher than the corresponding Percus-Yevick values (see Section 2.4.2.4).

The equimolar mixture is shown in Fig. 2.12 with a solid transition at about $\xi=0.49$ and $Z=6.9$. Similarly for the system with $x_2=0.8981$ of Fig. 2.13, the transition from the liquid to the solid occurs at a reduced density of $\xi=0.53$ and $Z=14.0$. These systems indicate that the Mansoori equation offers a good prediction of a binary hard sphere mixture's properties for fluid densities up to the solid transition even when the two spheres are very different in size.

A preliminary study of solid transitions in hard sphere mixtures is undertaken in the following section from an investigation of the system's dynamical and structural properties. The transport properties are analysed by following the self-diffusion coefficients of each component in the mixture, and the system's structure is examined with the help of the radial pair distribution functions.

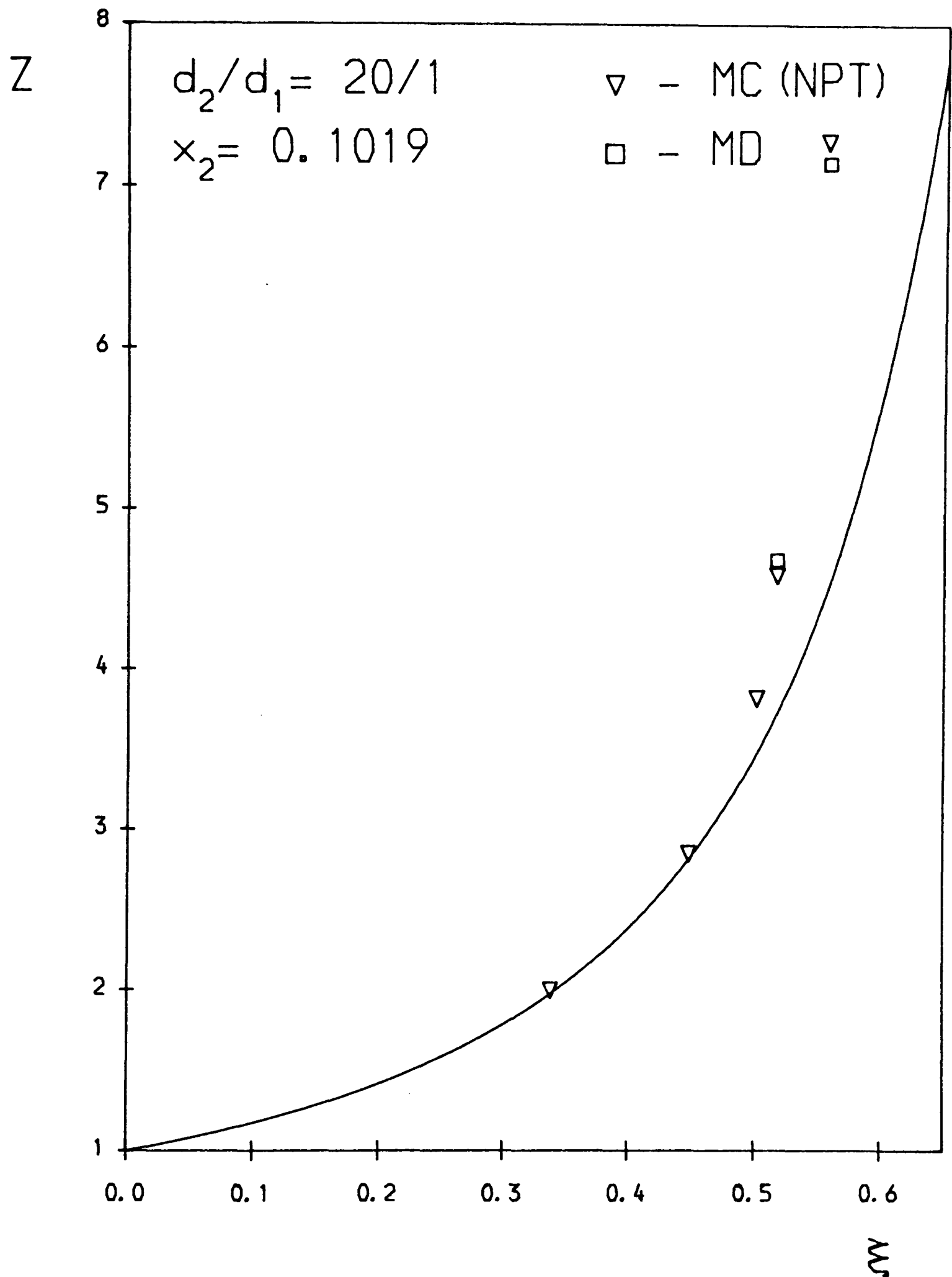


Fig. 2.11 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics results are represented by triangles and squares respectively, and the solid curve represents the Mansoori equation.

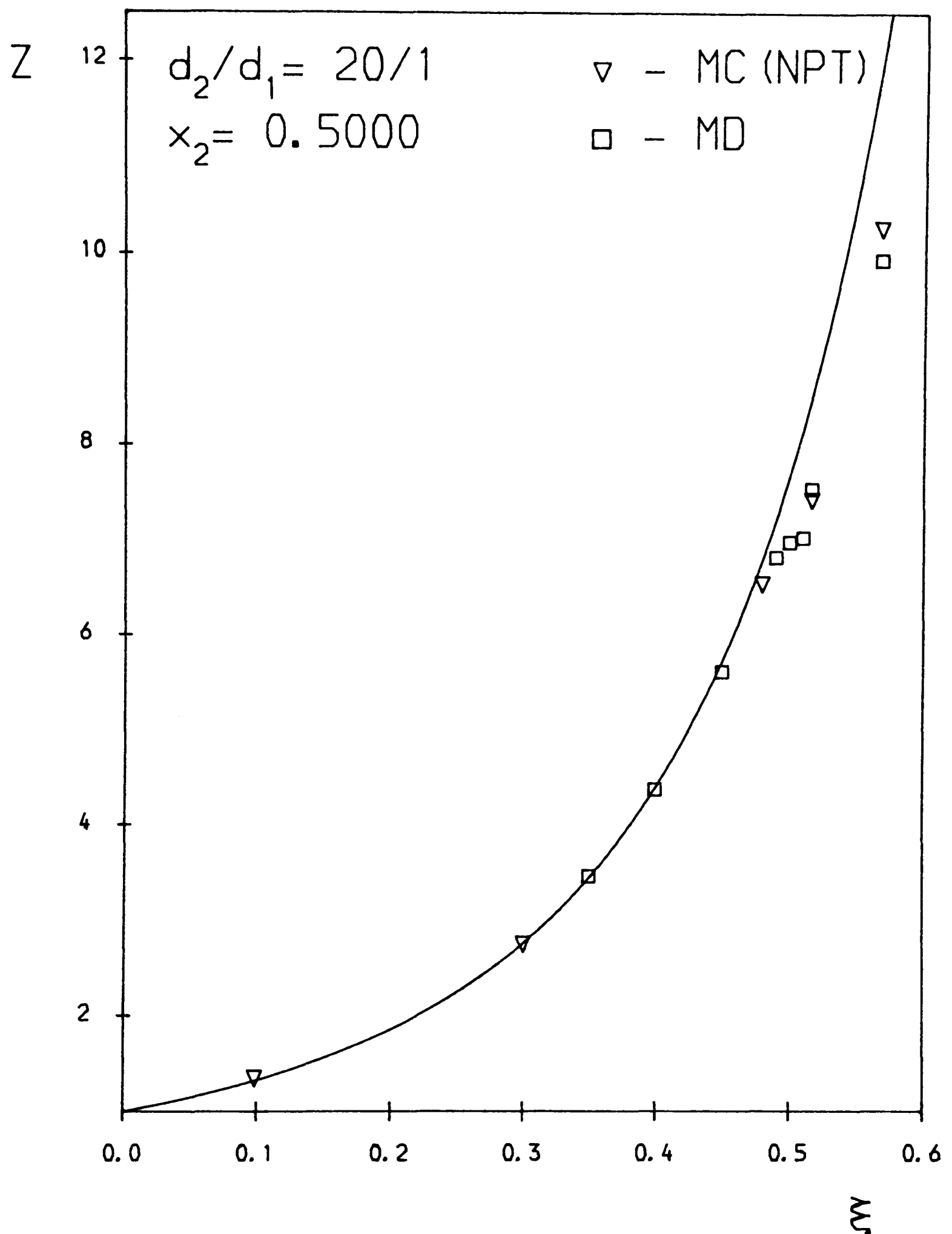


Fig. 2.12 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics results are the triangles and squares respectively.

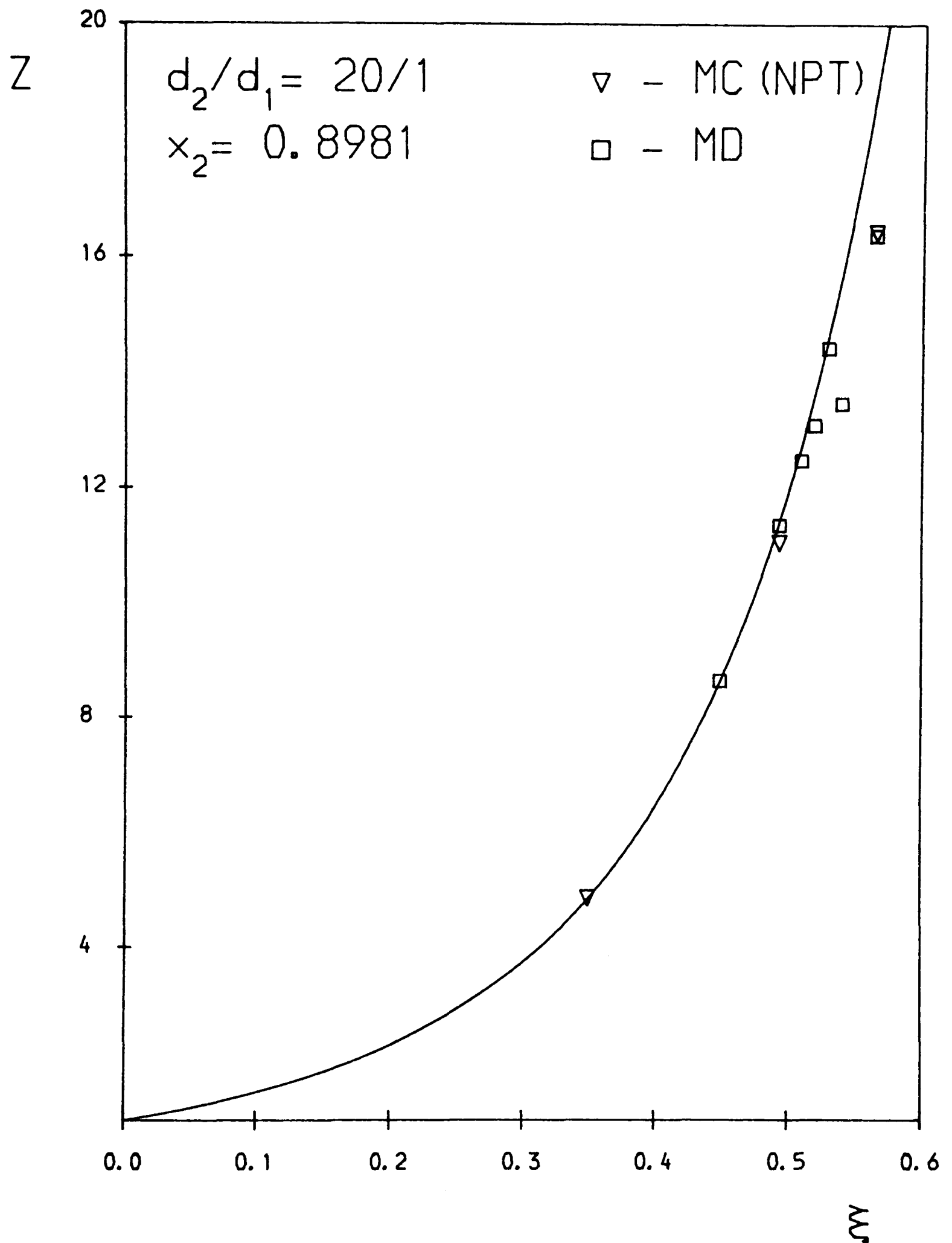


Fig. 2.13 The equation of state for a binary mixture of hard spheres. The NPT Monte Carlo and molecular dynamics data are the triangles and squares respectively, and the solid curve represents the Mansoori equation.

2.4.2 The Solid Transition

The study of a system's dynamical properties can provide an insight into its structural state. The root-mean-square, RMS, displacement as a function of time indicates the extent a particle has moved, and is obtained by taking the square root of the mean-square displacement, MSD. As described in Section 2.2, the self-diffusion coefficient can be obtained from the slope of the mean-square displacement by using the Einstein relation. An alternative route to the diffusion coefficient involves a time integration of the velocity autocorrelation function, but the oscillatory behaviour of the function's long tail usually results in a considerable error in evaluating the integral. In practice, the Einstein diffusion coefficients obtained from the molecular dynamics simulations presented in this section had a statistical error of the order of 5-10%. The diffusion coefficients calculated for the dilute species suffered considerably because of poor statistics.

For a fluid-like state, the particle's mean-square displacement will vary linearly with time, and the slope of the curve gives the value of the diffusion coefficient. However, in a solid-like state the particle's mean-square displacement will tend to oscillate about a mean value so that the net diffusion coefficient approaches zero. Thus by analysing the mean-square displacement for each species in the binary mixture during the course of the simulation it is possible to determine whether the system is in a liquid- or

solid-like state.

A more direct route to the structural state of the system is possible from a knowledge of the radial pair distribution function. The distribution functions can be used to determine the local short-range order in a fluid with the smooth peaks in the curve representing smeared out shells of first-nearest neighbours, second-nearest neighbours, etc. In a sense these peaks are remnants of the order found in the solid where the radial distribution function is represented by a series of sharp peaks. An evaluation of the distribution functions g_{11} , g_{12} , and g_{22} for binary hard sphere mixtures enables one to determine whether the system is in a fluid or solid state. Because obtaining the distribution functions using molecular dynamics is expensive in terms of computer time, the only system whose structure has been investigated in this way is the binary mixture with $d_2/d_1=20/1$.

The analytical solution for the radial distribution function of the Percus-Yevick equation for additive hard sphere mixtures was given by Lebowitz [10]. This method is tedious and can be greatly simplified by using Perram's reformulation of the Ornstein-Zernike equation [39]. In effect only a few tens of lines of computer code are required. However, the contact values of the distribution functions obtained from the Percus-Yevick equation using the method of Perram are too low compared with computer results, and the analytical solution oscillates out of phase with respect to the exact results. The usual Verlet-Weis

scheme [40] can then be used to correct these deficiencies, and the results are in good agreement with the computer data. Lee and Levesque [41] have summarized an equivalent Verlet-Weis fit upon the hard sphere solution given by Lebowitz.

2.4.2.1 System With $d_2/d_1=5/3$ -

The binary hard sphere mixture with $d_2/d_1=5/3$ at a mole fraction of $x_2=0.1019$ showed no solid transition even when the system's density was increased to about $\xi=0.6$. The root-mean-square displacement, RMS, for both the small, 1, and the large, 2, spheres at a density of $\xi=0.52$ are displayed in Fig. 2.14 in units of the diameter of the small sphere d_1 . t represents the absolute time in units of $\sqrt{(d_1^2 m/kT)}$. The corresponding mean-square displacements, MSD, for the two species are also shown in Fig. 2.14. It is clear that the plots of the mean-square displacement against time are virtually linear, indicating that the mixture is in a fluid state. An estimate of the diffusion coefficient D is obtained by fitting the best straight line through the data using a least squares procedure the slope of which gives $6D$. The variation of the diffusion coefficients of species 1, D_1 , and species 2, D_2 , with density is shown in Fig. 2.15. The transport coefficients decrease continuously as the density is increased indicating that no abrupt phase transition has occurred.

The root-mean-square displacement, RMS, and mean-square displacement, MSD, for both species in an equimolar $x_2=0.5$

mixture with $d_2/d_1=5/3$ are displayed in Fig. 2.16 at a density of $\xi=0.54$. As expected from the results in Section 2.4.1.2, the motion corresponds to a system in a liquid-like state. The fact that no transition occurs is consistent with the smooth variation of the diffusion coefficients with increasing density (Fig. 2.17).

A transition from a liquid state to a solid state is seen for the system with $d_2/d_1=5/3$ at a higher mole fraction of the larger spheres, $x_2=0.8981$. Fig. 2.18 shows the root-mean-square and mean-square displacements for a density of $\xi=0.48$ in a liquid state, and Fig. 2.19 displays the results for a solid density $\xi=0.6$ above the phase transition. The mean-square displacements, MSD, of the small, 1, and large, 2, species vary virtually linearly with time when the system is in a liquid state as seen in Fig. 2.18. However, it is clear from Fig. 2.19 for a density corresponding to the solid phase that the mean-square displacements of both species 1 and 2 oscillate about a mean value indicating that both types of spheres have frozen into a crystal lattice.

The liquid-solid phase transition for this mixture with $x_2=0.8981$ is characterized by a discontinuity in the variation of the diffusion coefficients as shown in Fig. 2.20. The diffusion coefficients of species 1 and 2 show a discontinuity at the transition density of $\xi=0.52$ beyond which they effectively become zero as the whole system solidifies. The abrupt behaviour of the diffusion coefficient can be used to locate the transition density.

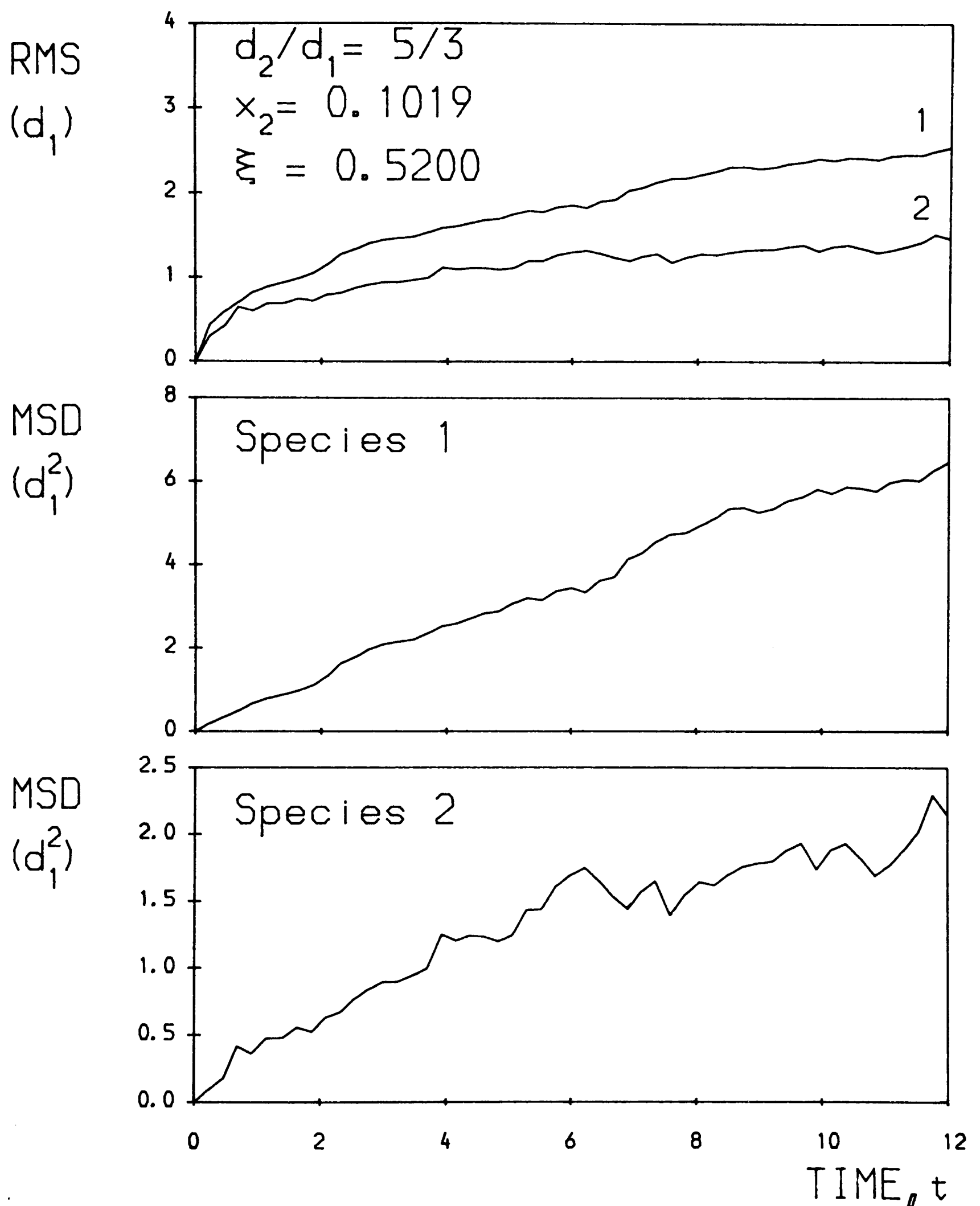


Fig. 2.14 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

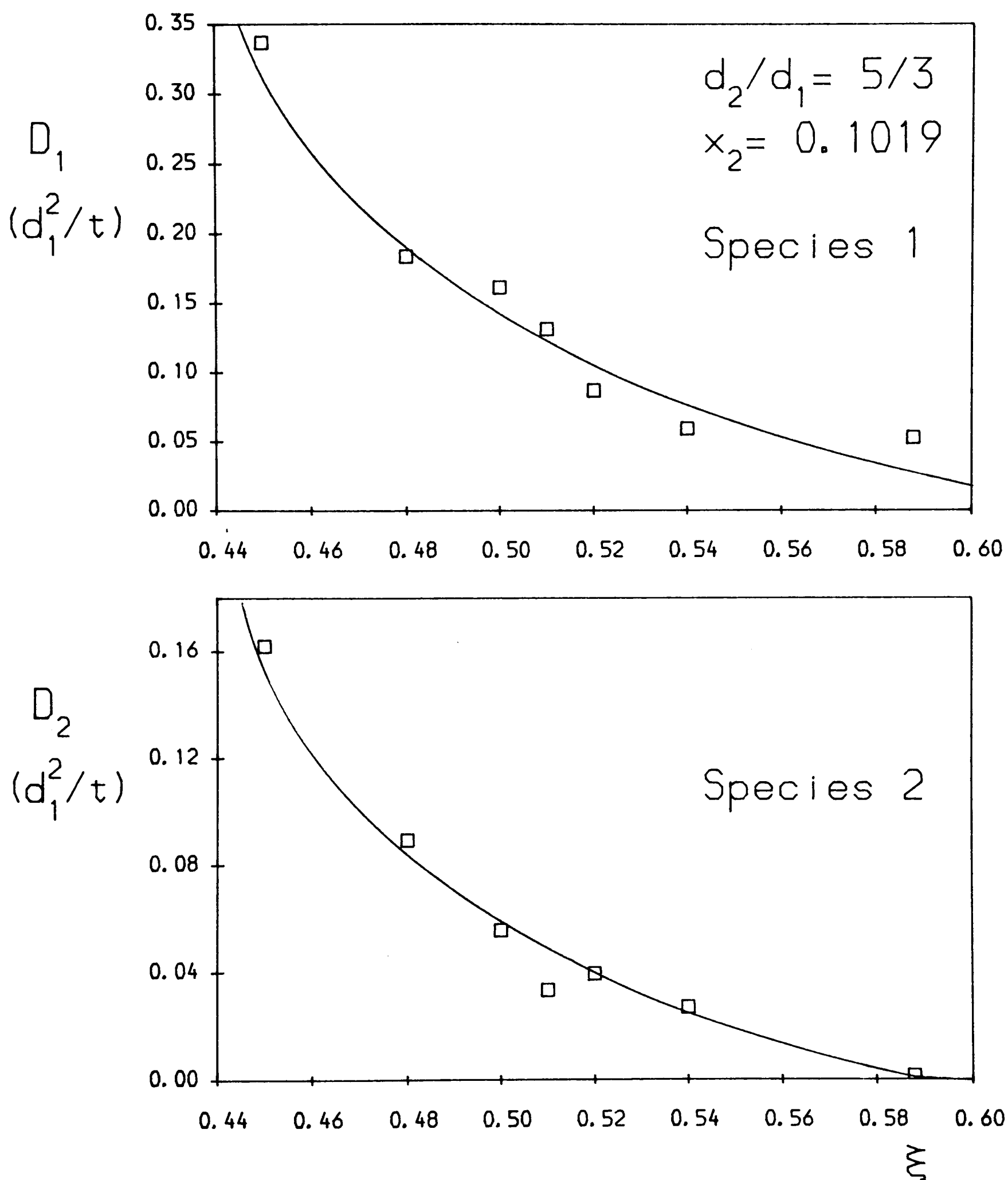


Fig. 2.15 The self-diffusion coefficients of species 1, D_1 , and species 2, D_2 , as a function of density, ξ , for a binary mixture of hard spheres.

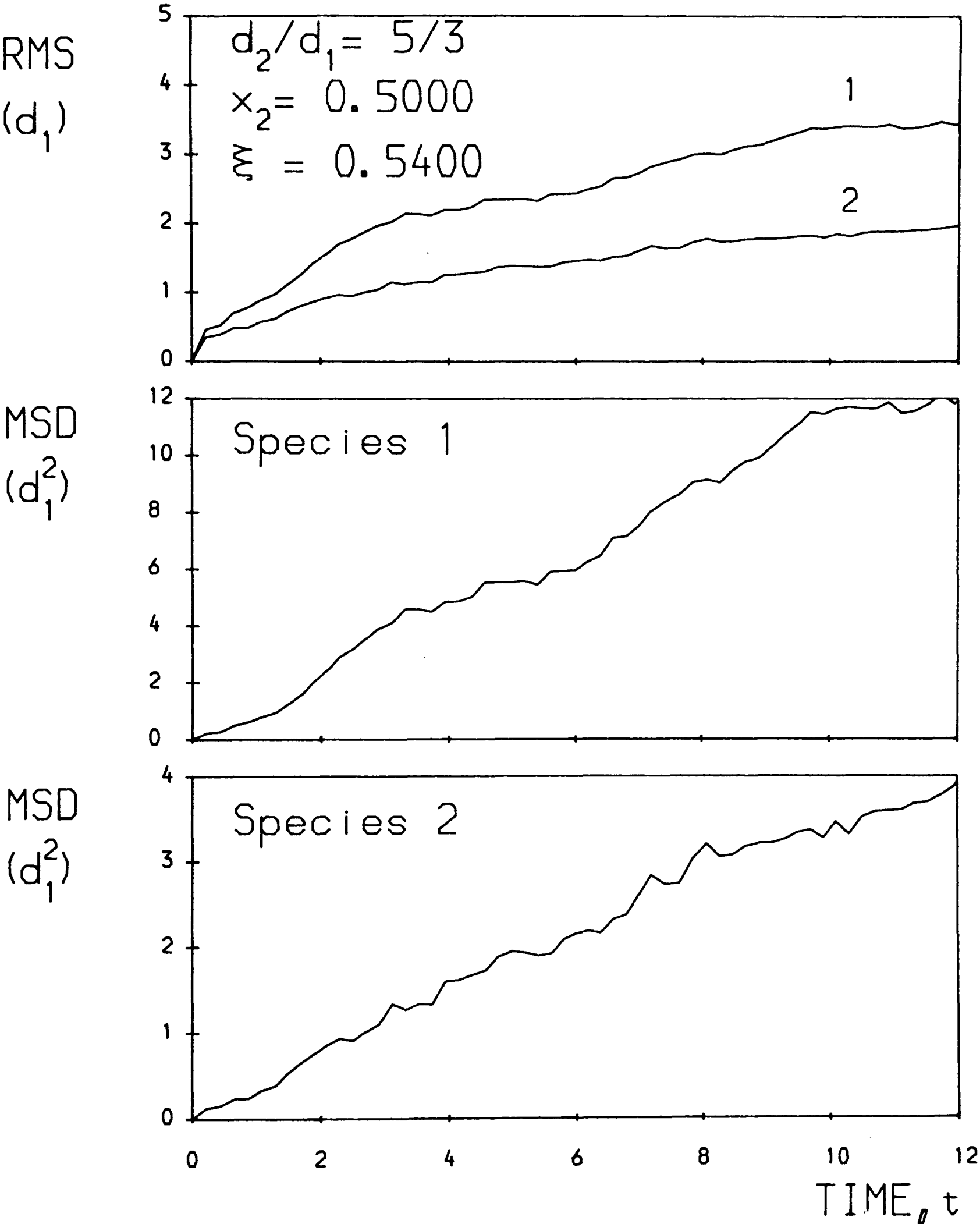


Fig. 2.16 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

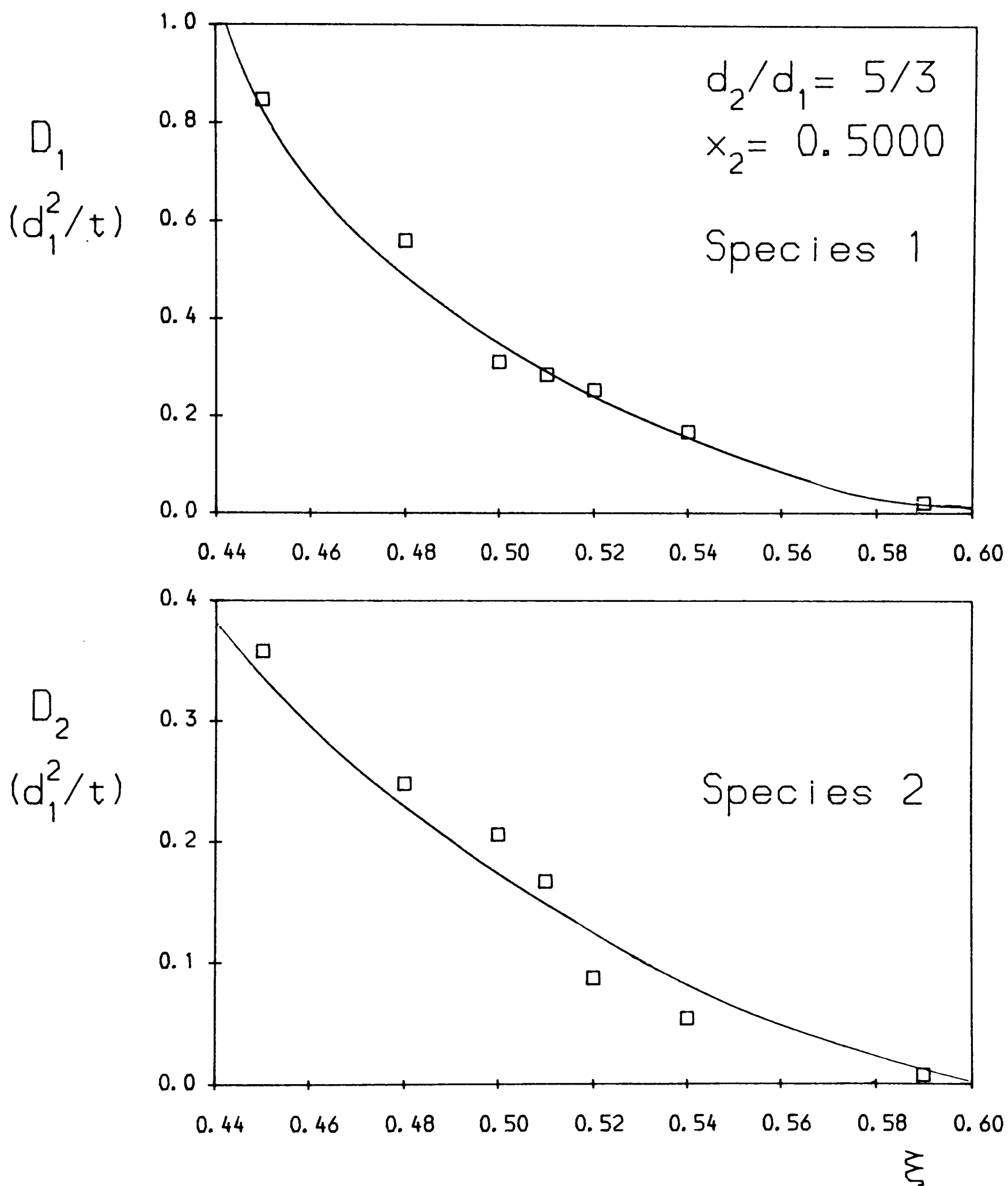


Fig. 2.17 The self-diffusion coefficients of species 1, D_1 , and species 2, D_2 , as a function of density, ξ , for a binary mixture of hard spheres.

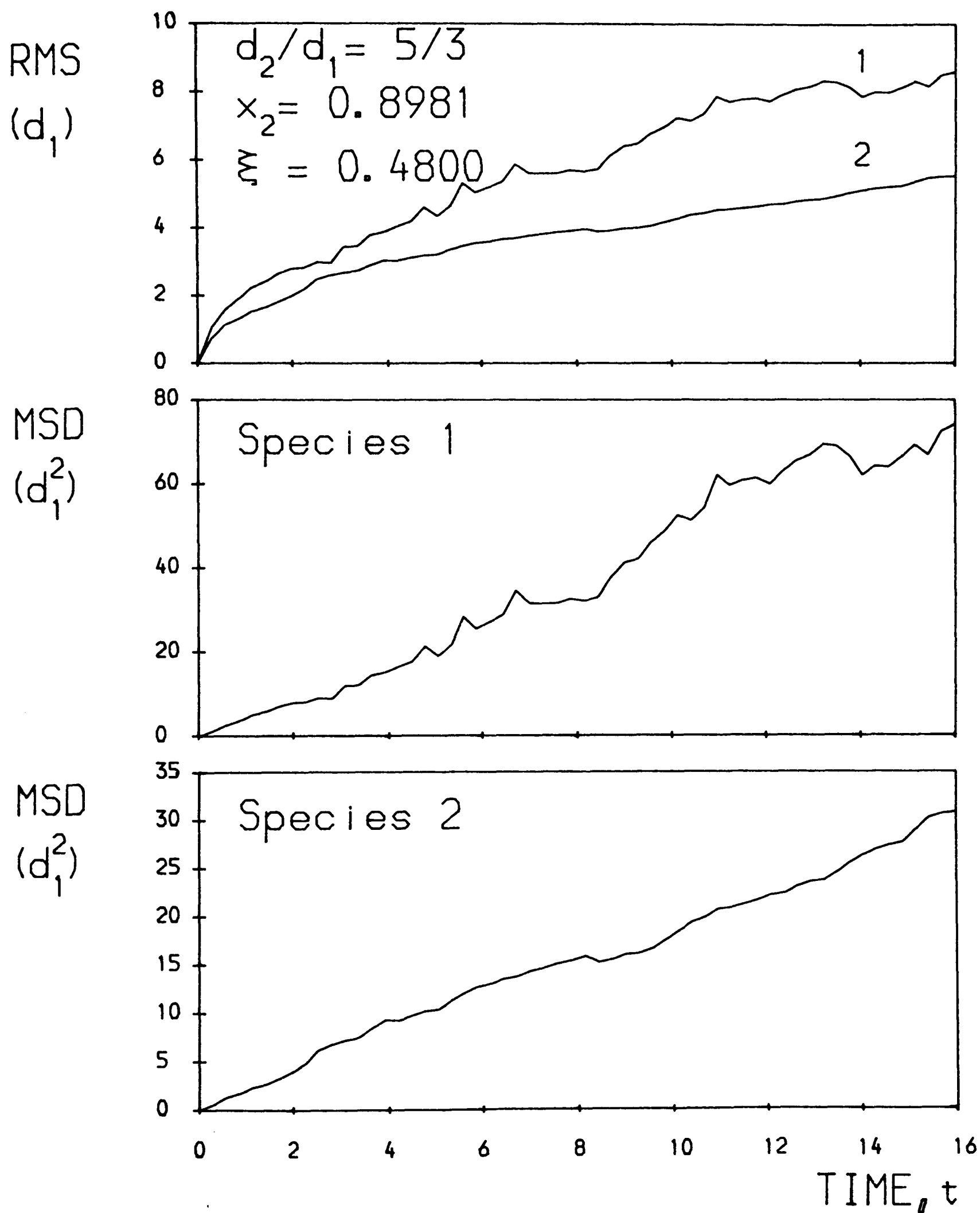


Fig. 2.18 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

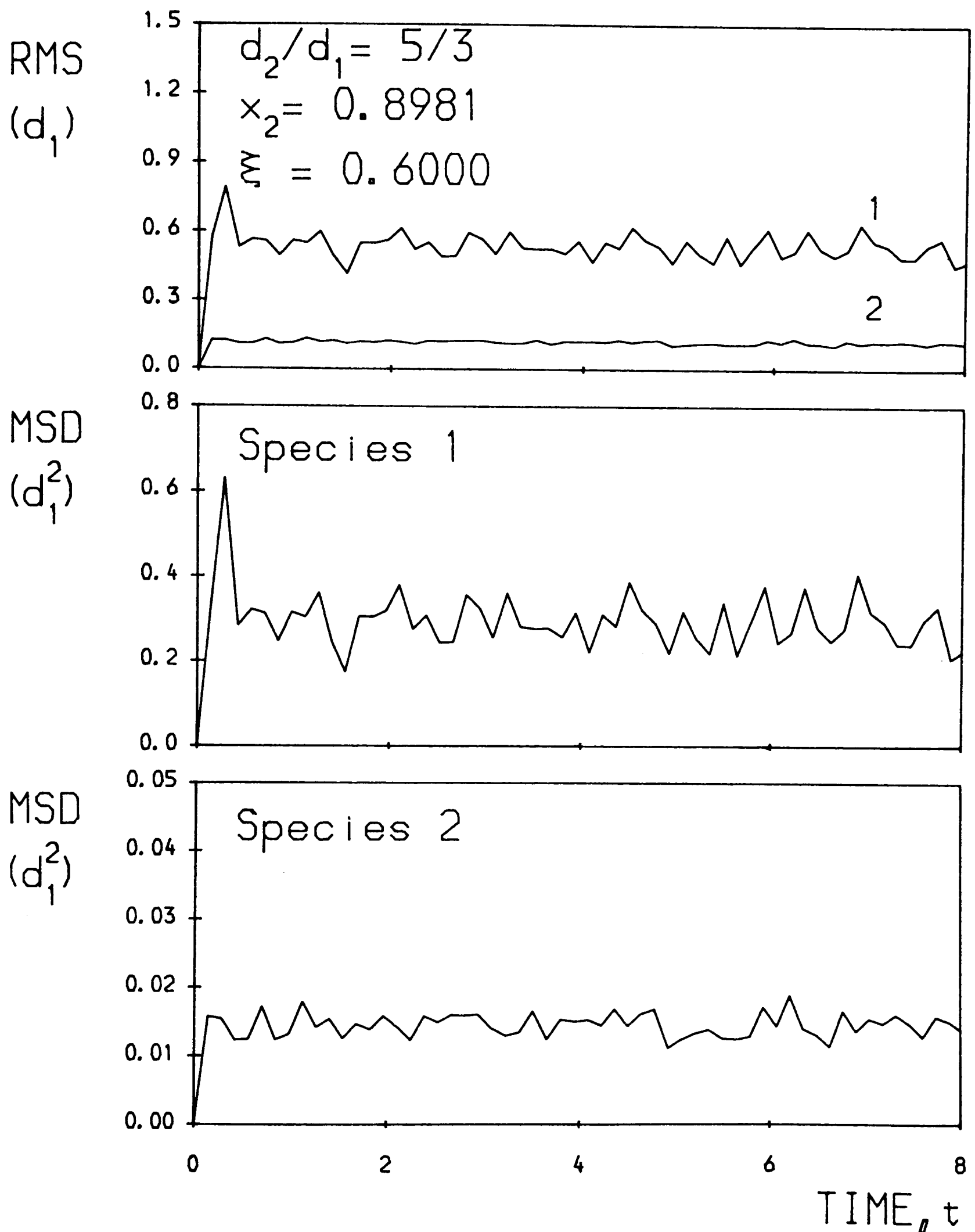


Fig. 2.19 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

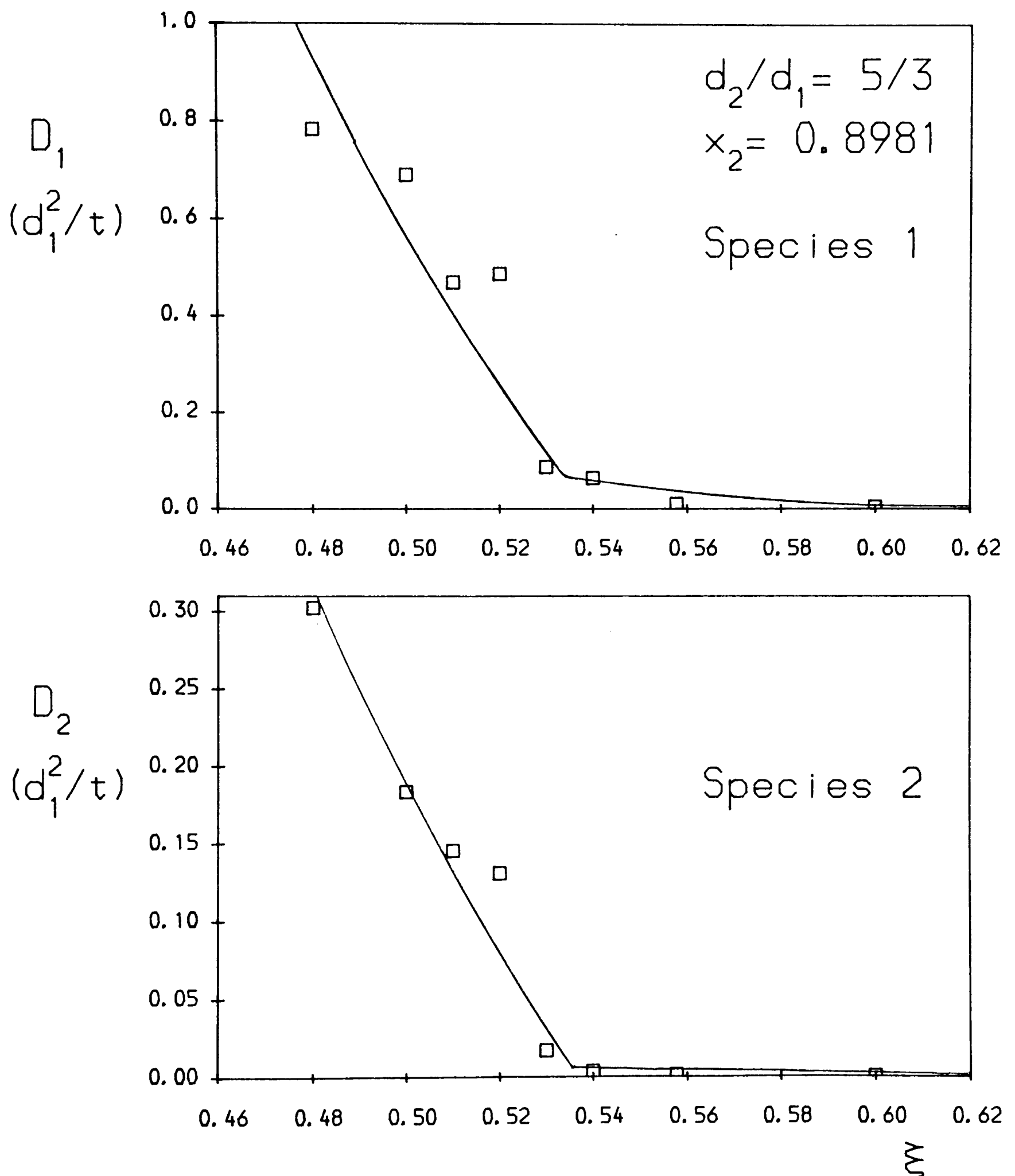


Fig. 2.20 The self-diffusion coefficients of species 1, D_1 , and species 2, D_2 , as a function of density, ξ , for a binary mixture of hard spheres.

2.4.2.2 System With $d_2/d_1=3/1$ -

The behaviour of a mixture of hard spheres with a diameter ratio of $d_2/d_1=3/1$ is qualitatively similar to the mixture with $d_2/d_1=5/3$ described in the previous section. At mole fractions of $x_2=0.0648$ and $x_2=0.5$, the mixture remains fluid-like even at high densities as shown in Fig. 21 and Fig. 22 respectively, and no transition to the solid is seen.

However, when the composition of the large spheres is increased to a value of 0.8981, a solid transition occurs at a density of about $\xi=0.53$. Fig. 23 displays the root-mean-square and mean-square displacements of each species for a liquid density of $\xi=0.45$. As expected the motion of the small and the large spheres is liquid-like. At a density of $\xi=0.6009$ above the solid transition, the root-mean-square displacement of species 2 obtains solid-like characteristics as the large spheres freeze into a crystal lattice (see Fig. 2.24). It appears that the smaller species 1 is still free to move between the spaces of the lattice formed by the large spheres although the motion is severely impeded causing the small sphere to remain at given lattice sites for a moderate amount of time. The corresponding discontinuity in the diffusion coefficient of species 2 at the liquid-solid transition density of $\xi=0.53$ can be seen in Fig. 2.25. Unlike the mixture with $d_2/d_1=5/3$ and $x_2=0.8981$ the diffusion coefficient of species 1 does not become zero at the transition density, although the transport coefficient for species 2 does.

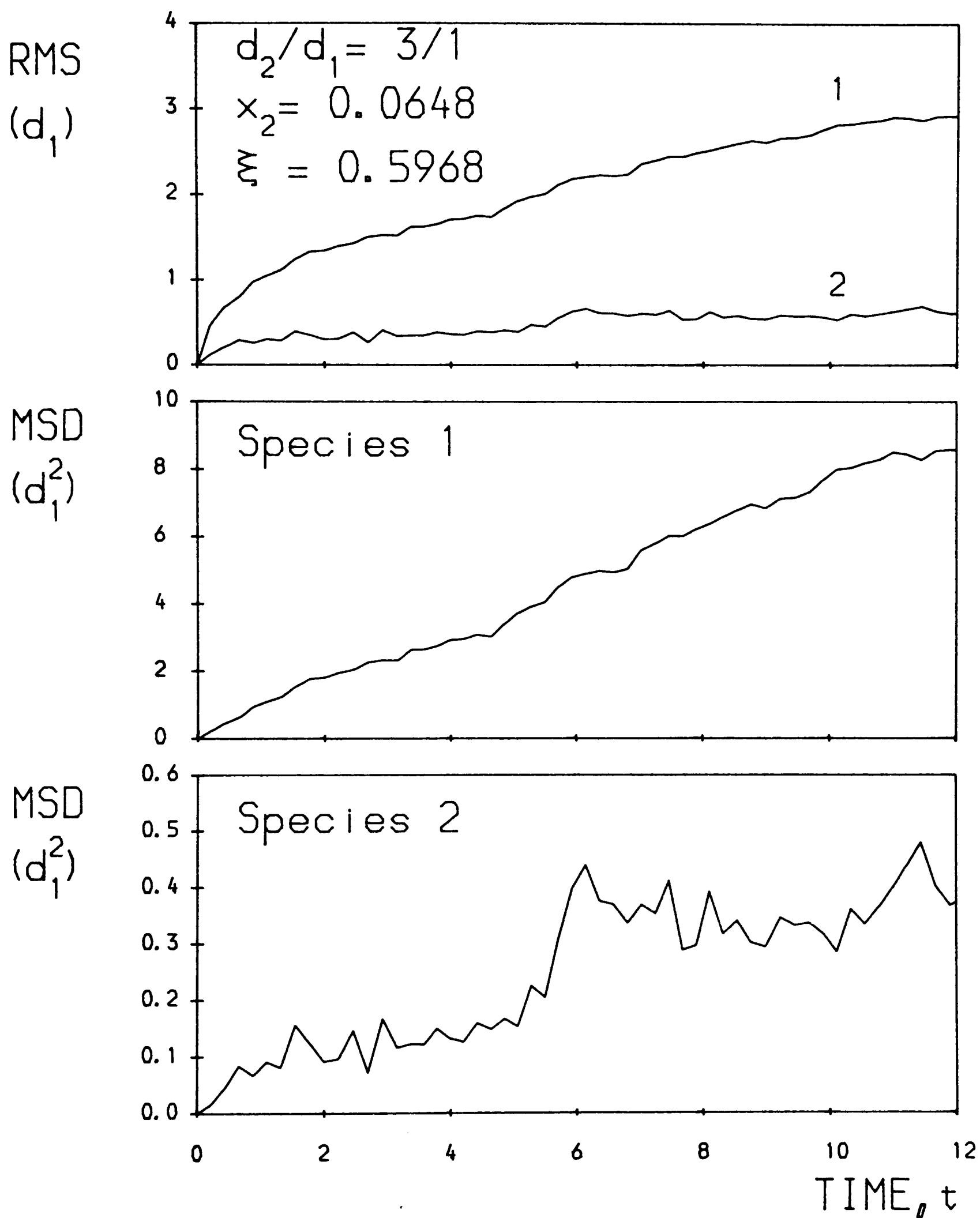


Fig. 2.21 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

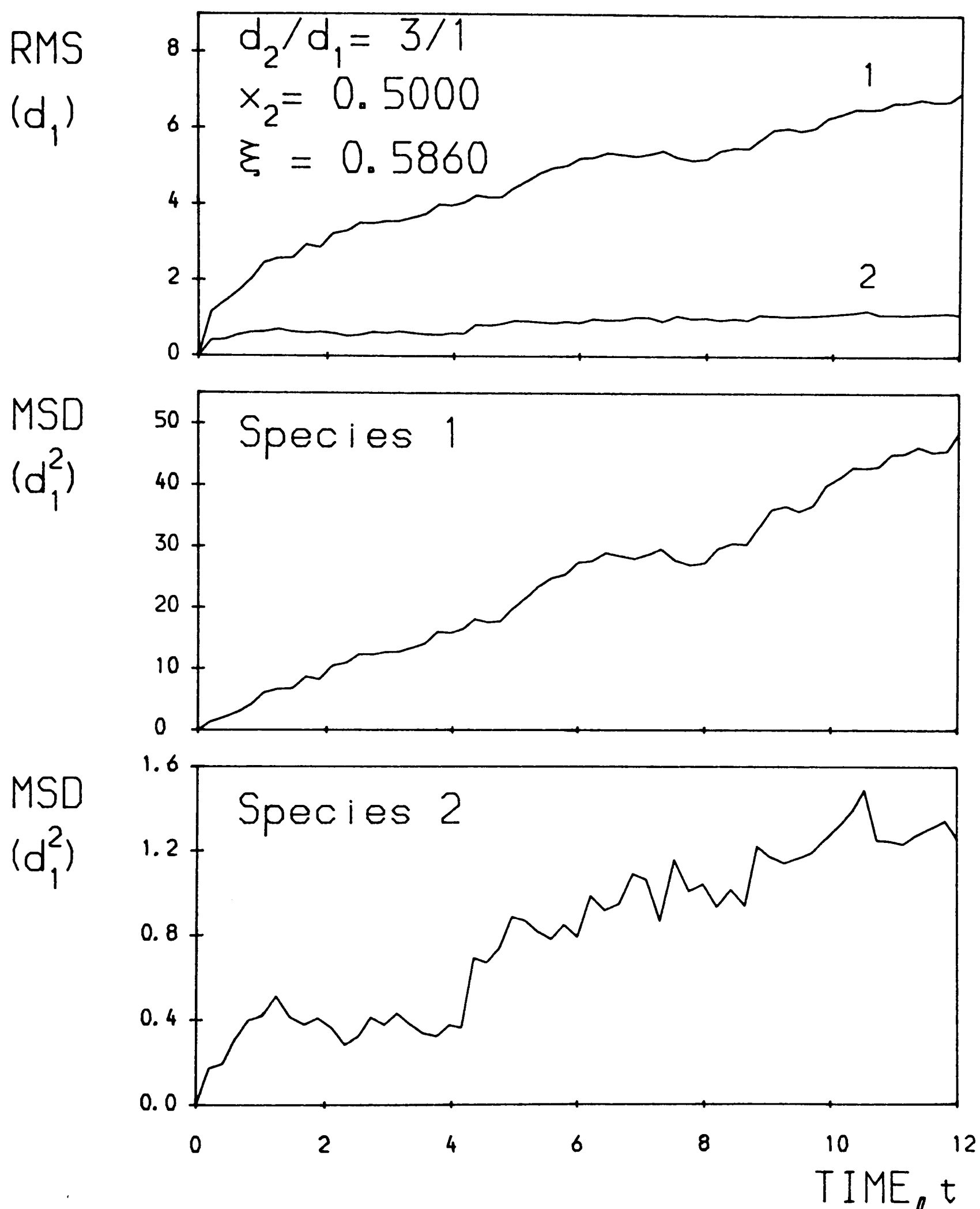


Fig. 2.22 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

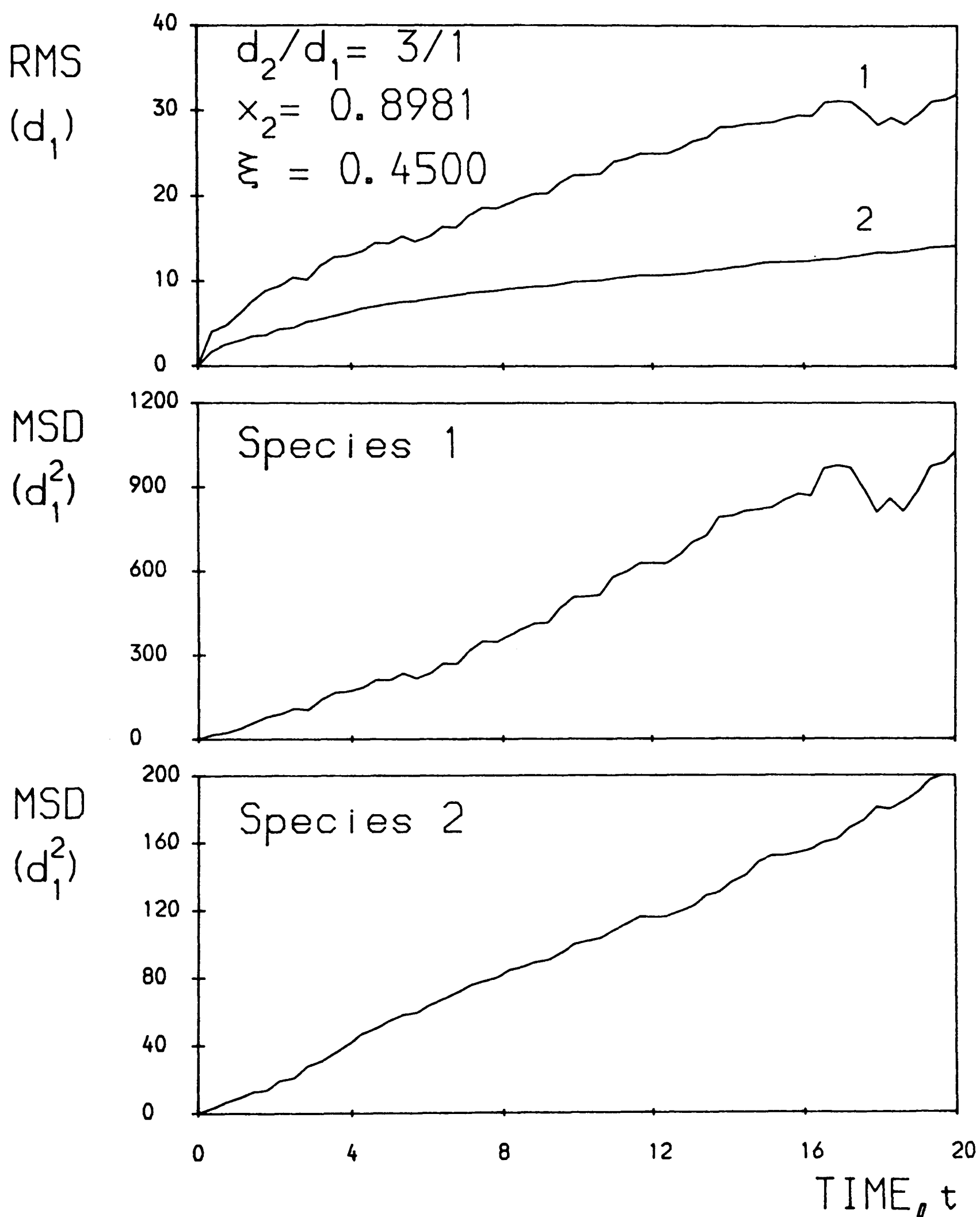


Fig. 2.23 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

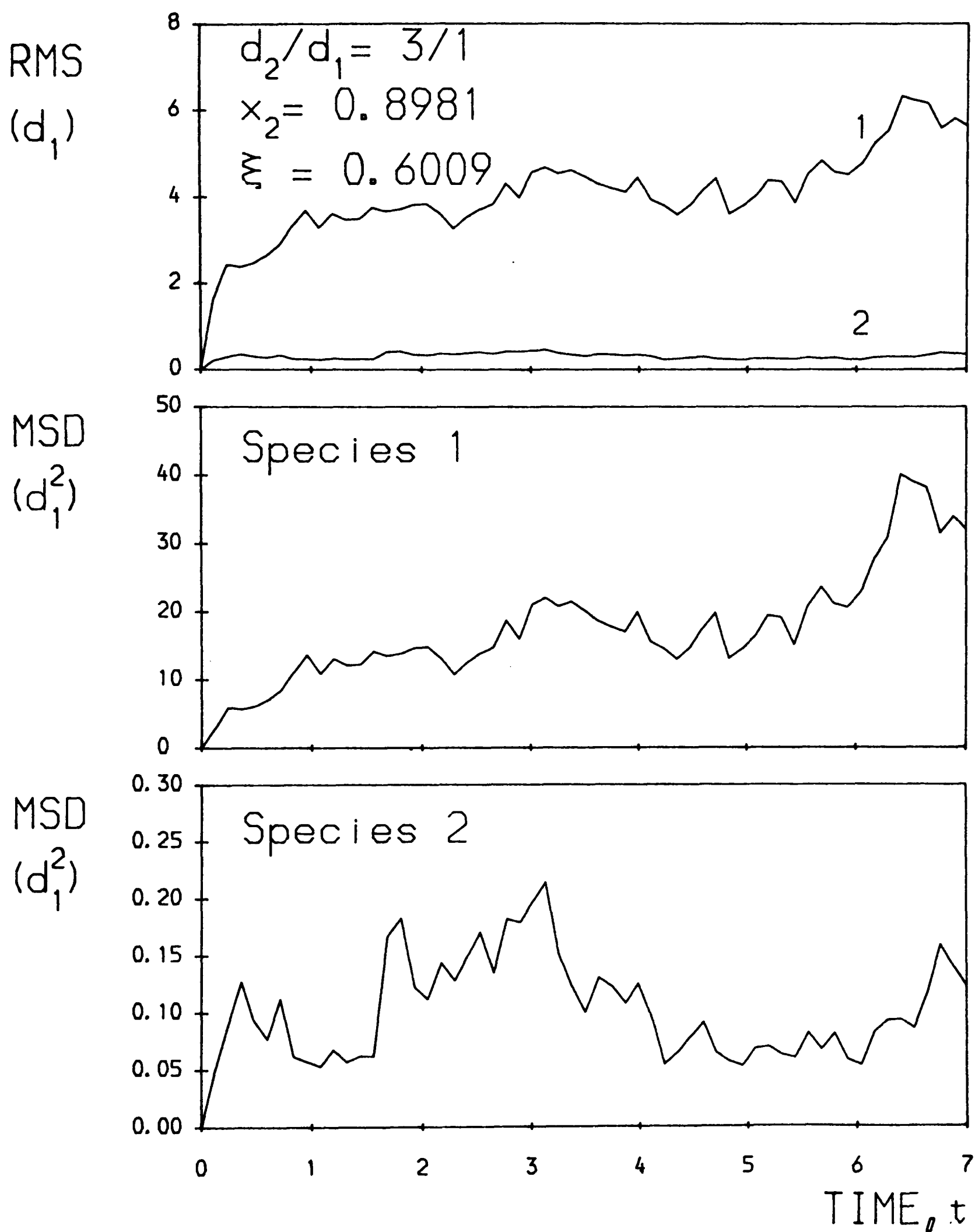


Fig. 2.24 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

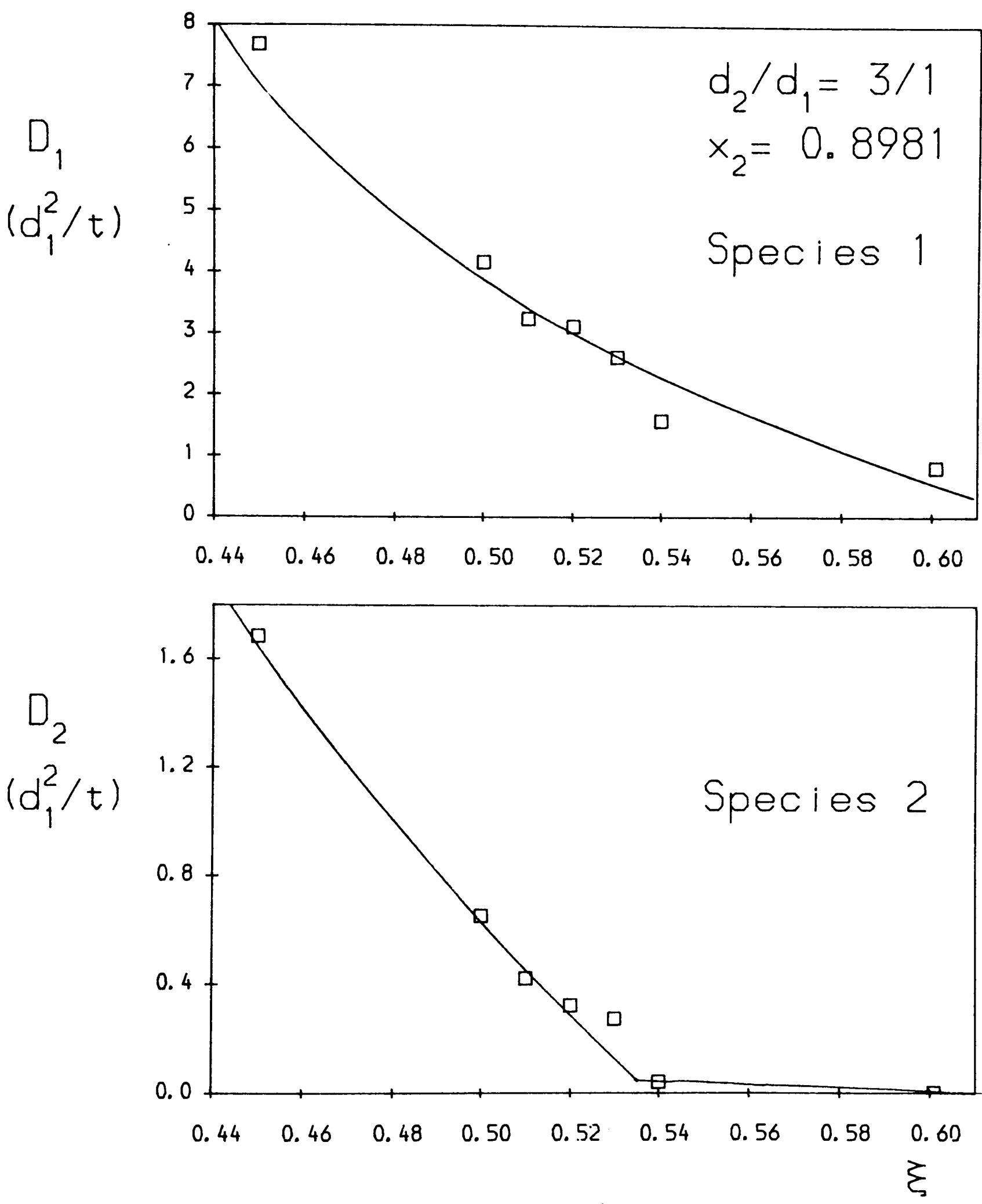


Fig. 2.25 The self-diffusion coefficients of species 1, D_1 , and species 2, D_2 , as a function of density, ξ , for a binary mixture of hard spheres.

2.4.2.3 System With $d_2/d_1=5/1$ -

The solid transition is not seen in simulations of the $d_2/d_1=5/1$ hard sphere mixture when a large proportion of the spheres are small. Fig. 2.26 displays the dynamical properties of a system with a mole fraction of $x_2=0.1019$ at a density of $\xi=0.5575$. The motion of the particles remains liquid-like even at high densities.

Fig. 2.27 shows the root-mean-square and mean-square displacements for an equimolar mixture $x_2=0.5$ at a reduced density of $\xi=0.45$. This corresponds to a state along the liquid branch of the curve in Fig. 2.9. This mixture exhibits a transition from a liquid to a solid phase at a density of about $\xi=0.52$, and Fig. 2.28 represents a solid density of $\xi=0.5747$ above the transition point. Although the small spheres 1 move quite freely, the large spheres 2 are confined to a solid lattice with the characteristic oscillation of the mean-square displacement about an average value. The small but non-negligible overall diffusion of the large particles is apparently due to lattice dislocations when the particle moves sharply from one position in the lattice to another. The density of the phase transition is represented by the characteristic discontinuity in the diffusion coefficient D_2 as seen in Fig. 2.29.

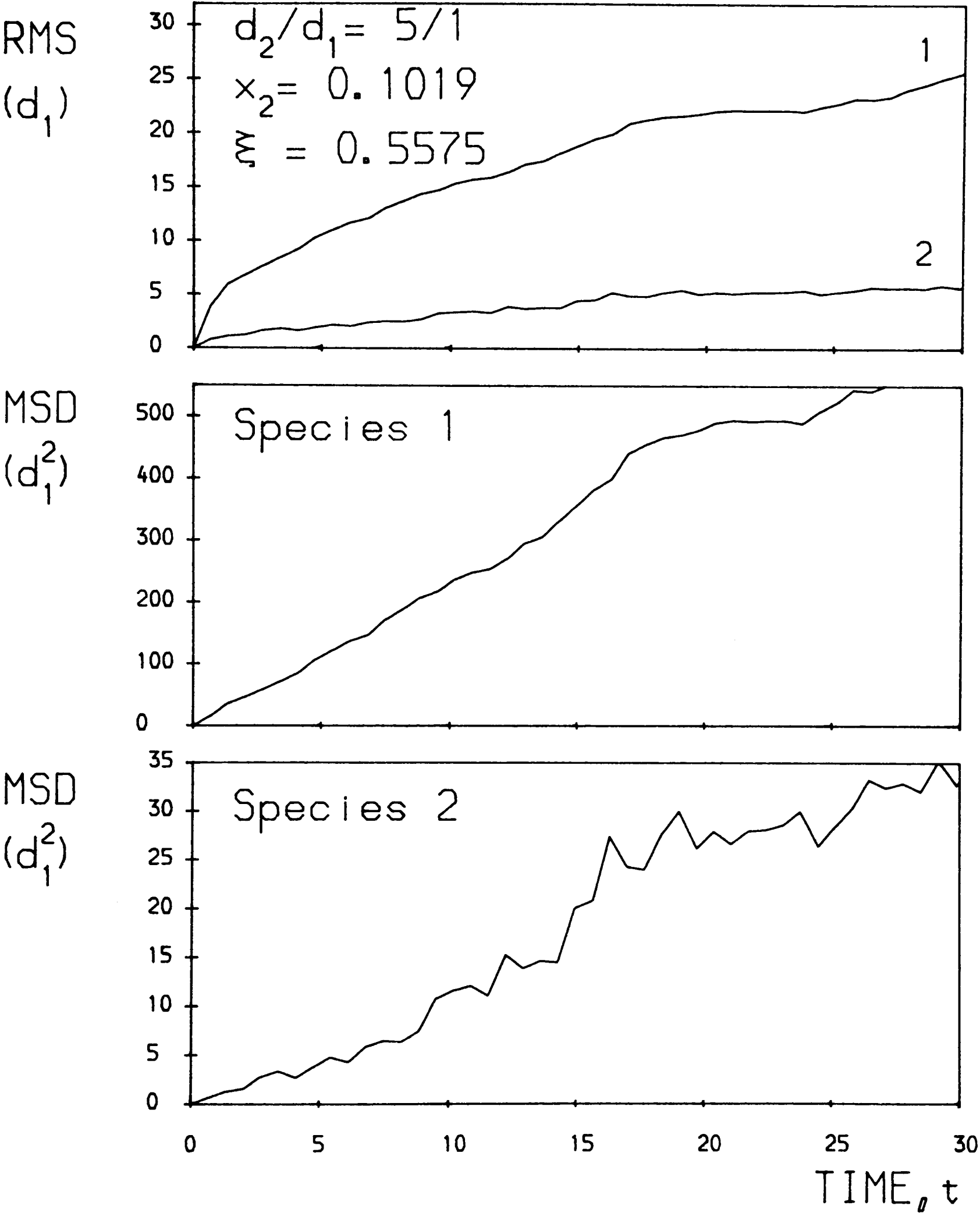


Fig. 2.26 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

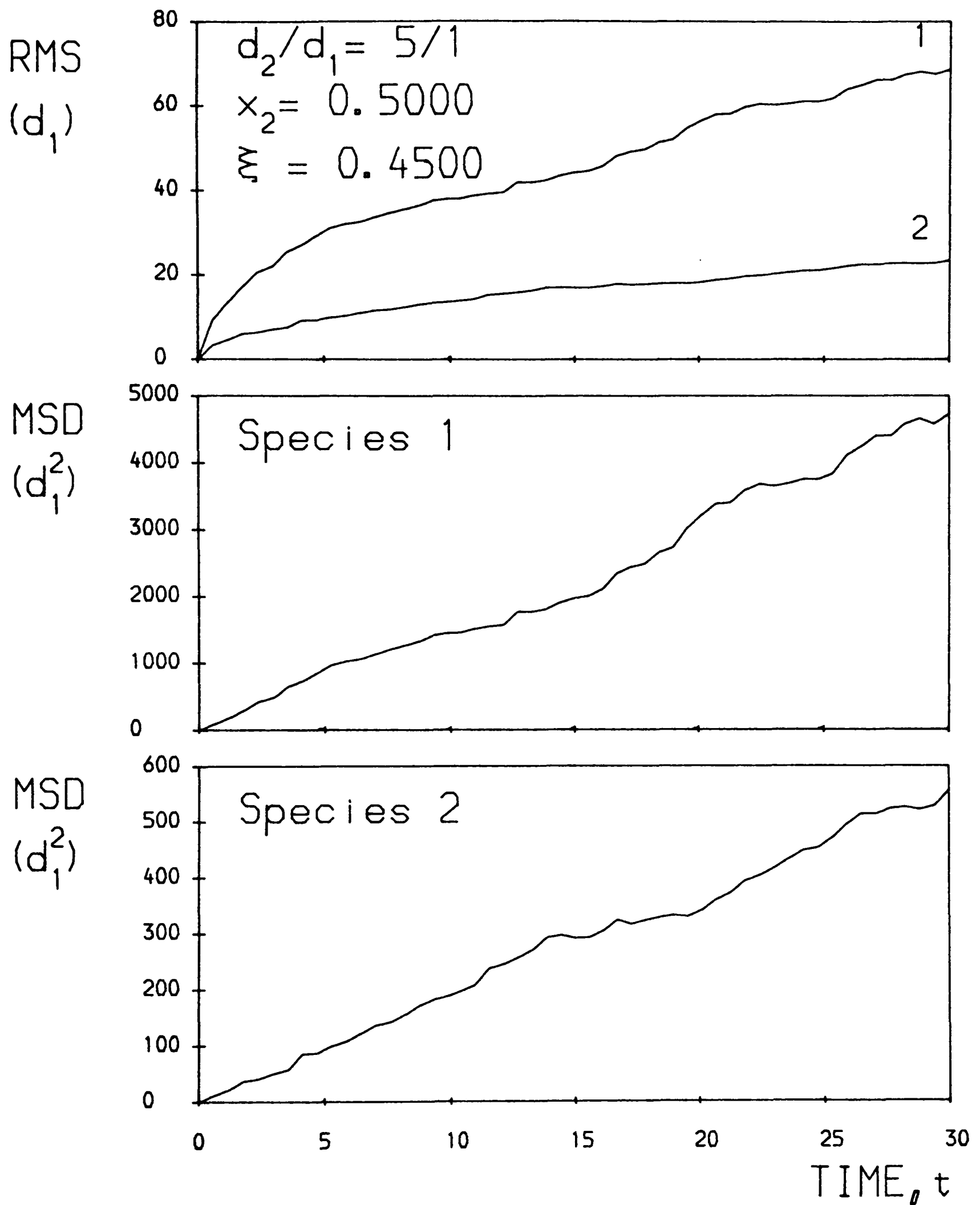


Fig. 2.27 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

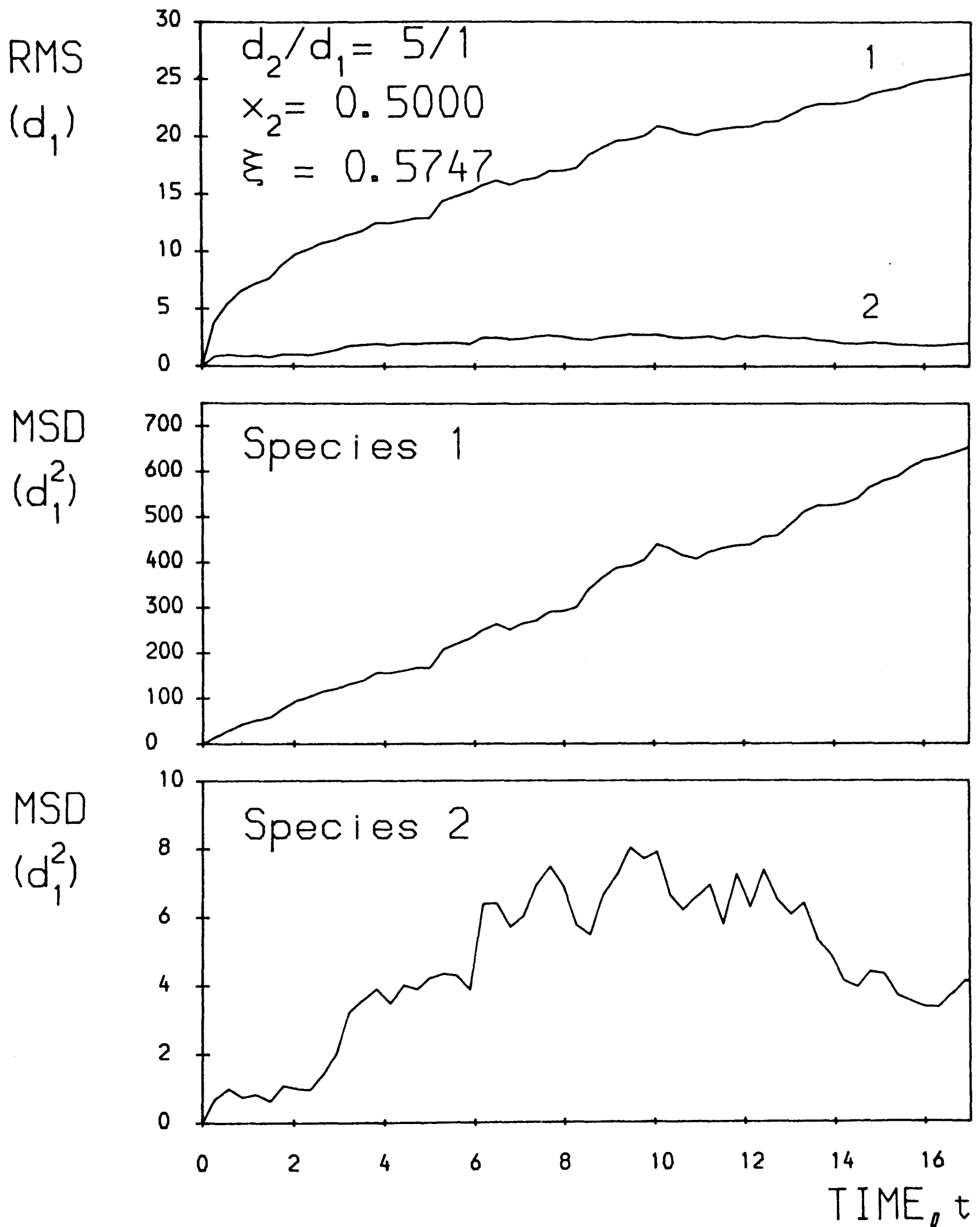


Fig. 2.28 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

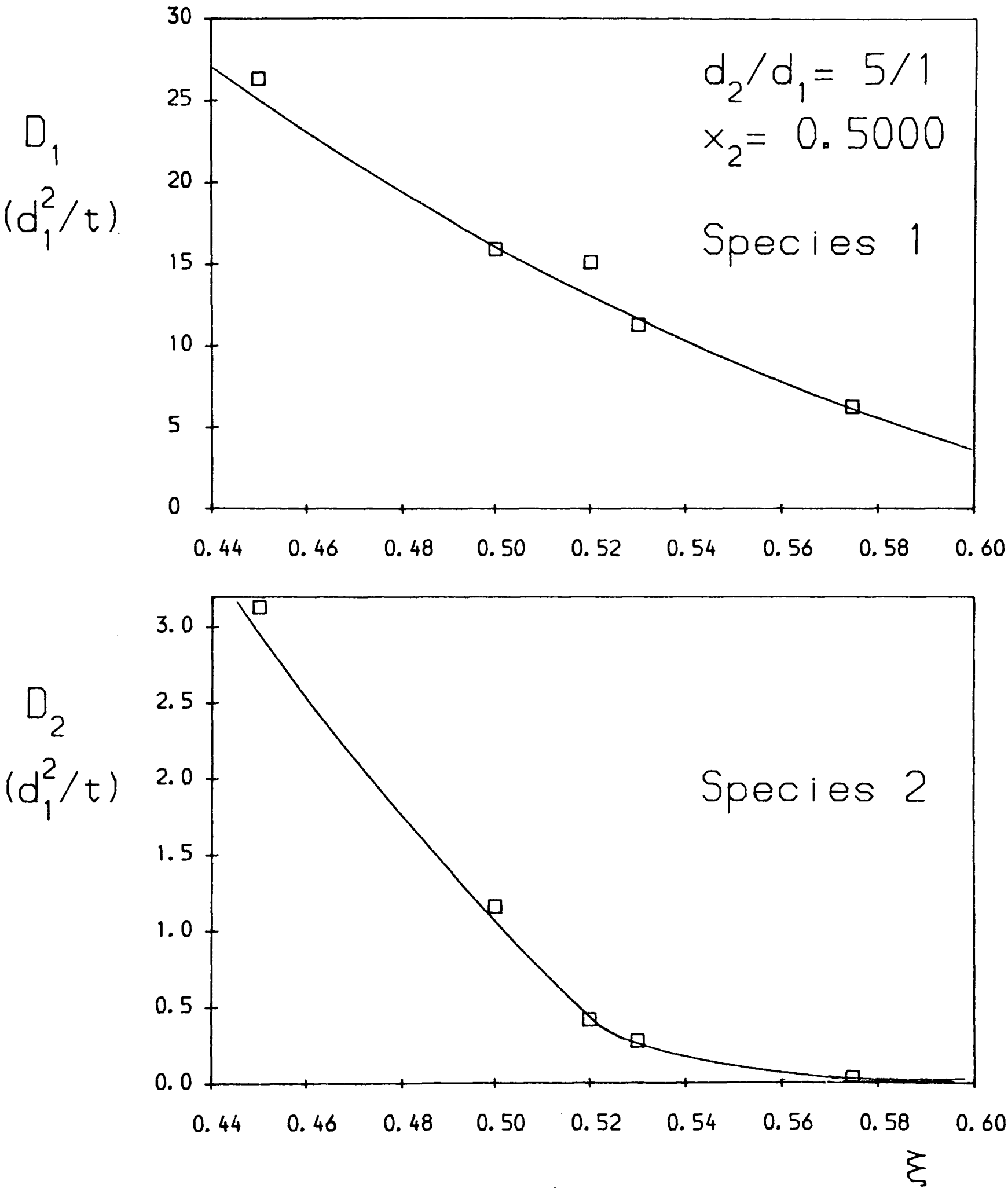


Fig. 2.29 The self-diffusion coefficients of species 1, D_1 , and species 2, D_2 , as a function of density, ξ , for a binary mixture of hard spheres.

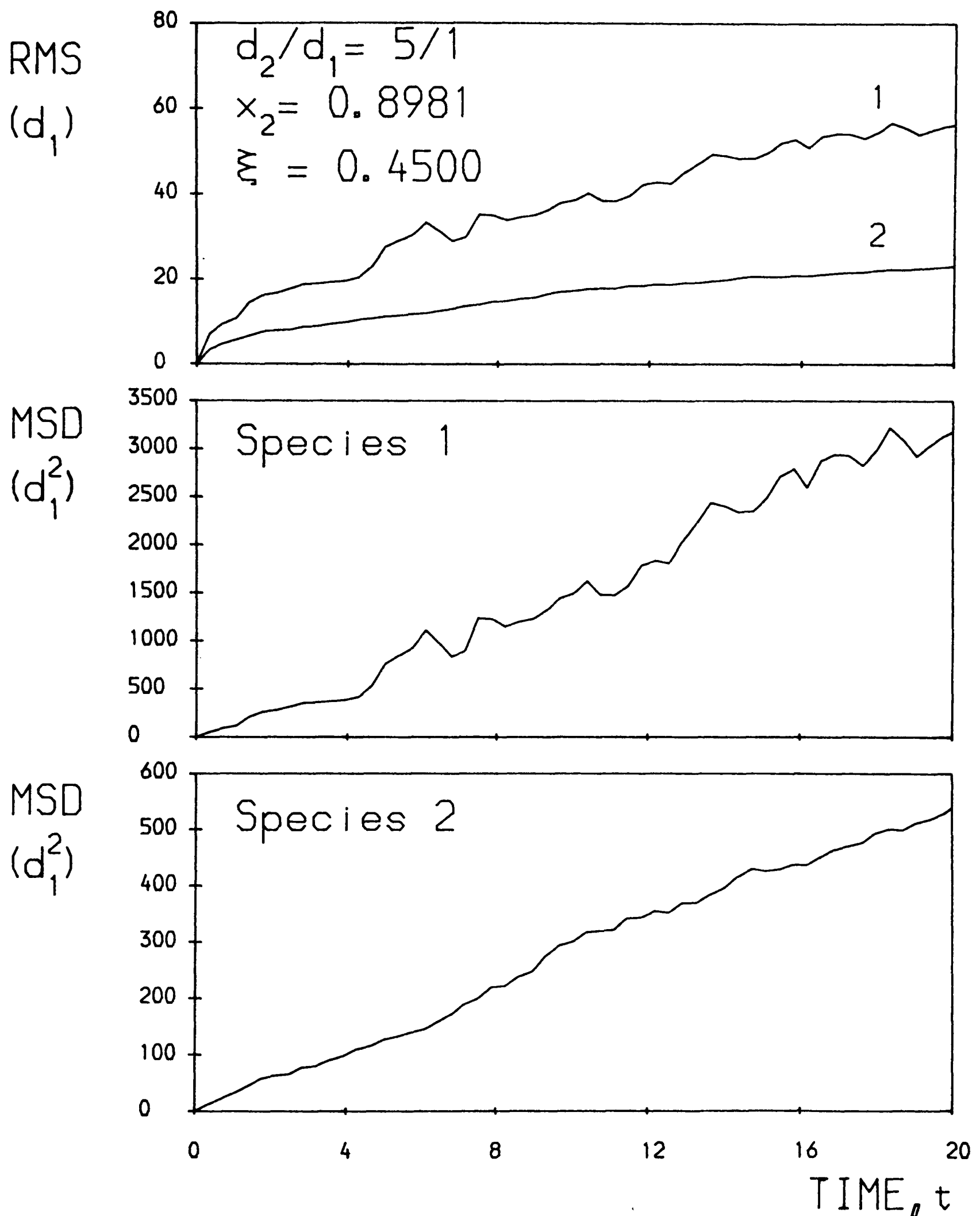


Fig. 2.30 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

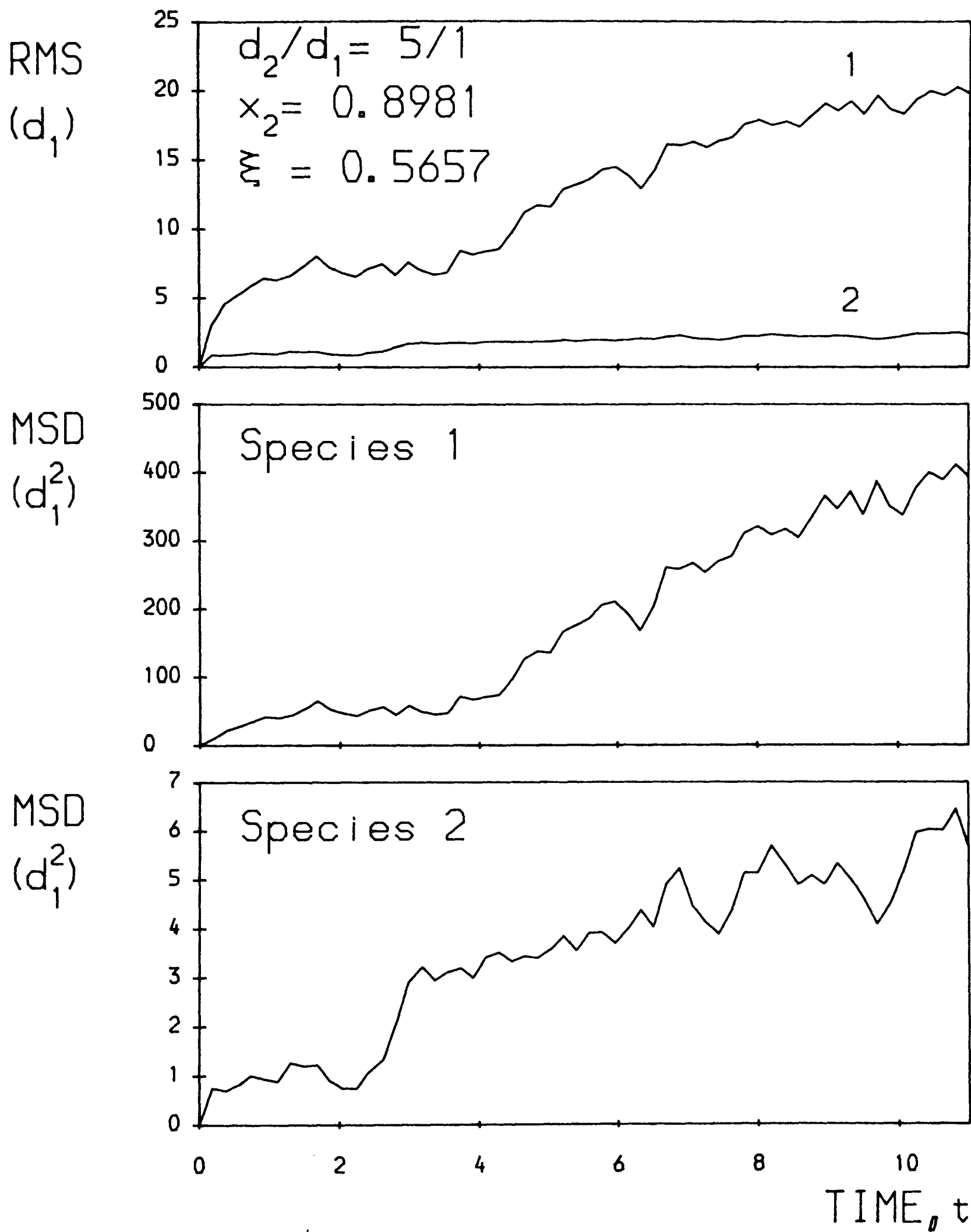


Fig. 2.31 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

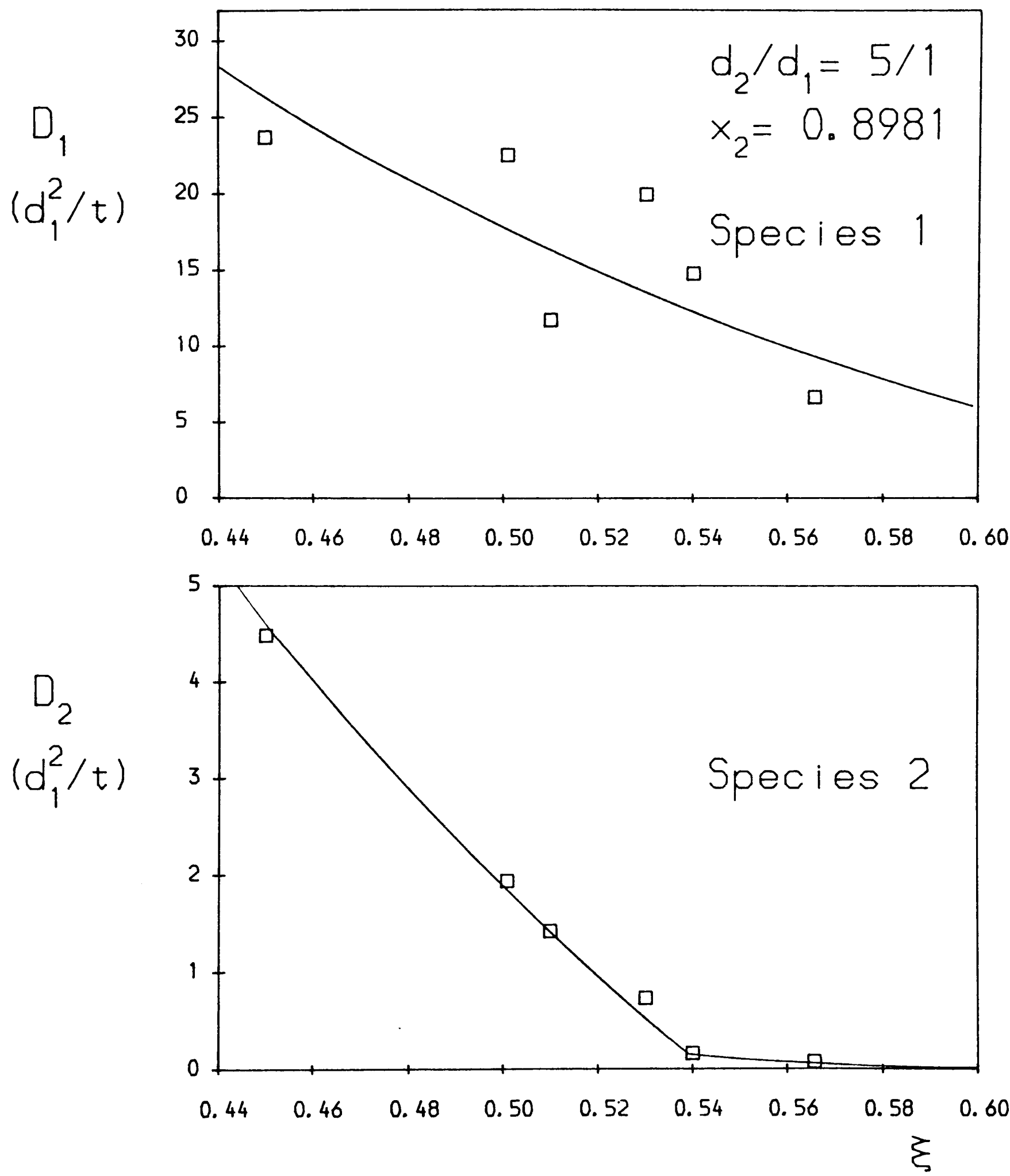


Fig. 2.32 The self-diffusion coefficients of species 1, D_1 , and species 2, D_2 , as a function of density, ξ , for a binary mixture of hard spheres.

The $d_2/d_1=5/1$ hard sphere mixture corresponding to a mole fraction of $x_2=0.8981$ also displays a solid transition. Fig. 2.30 and Fig. 2.31 display the motion of the particles for densities representing a liquid state, $\xi=0.45$, and solid state, $\xi=0.5657$, respectively. The transition from liquid to solid occurs at a density of $\xi=0.53$ corresponding to the break in the transport coefficient of species 2 seen in Fig. 2.32, indicating that the small spheres move in the spaces of the lattice formed by the large spheres.

2.4.2.4 System With $d_2/d_1=20/1$ -

The solid transitions occurring in binary hard sphere mixtures with a diameter ratio of $d_2/d_1=20/1$ are investigated in this section. The results of the dynamical studies are complemented with an investigation of the system's structure from an analysis of the radial distribution functions. The solid curves in the figures for the radial distribution functions are obtained using Perram's method with a Verlet-Weis type correction. The corresponding distribution functions obtained from molecular dynamics simulations are represented by squares.

When the proportion of the large spheres in the mixture is relatively small, no transition to the solid is observed. The system with a mole fraction of $x_2=0.1019$ does not attain any solid-like structure even at high densities. The mean-square displacements for each species at a density of $\xi=0.5580$ shown in Fig. 2.33 suggest that the particles are free to move in a fluid environment.

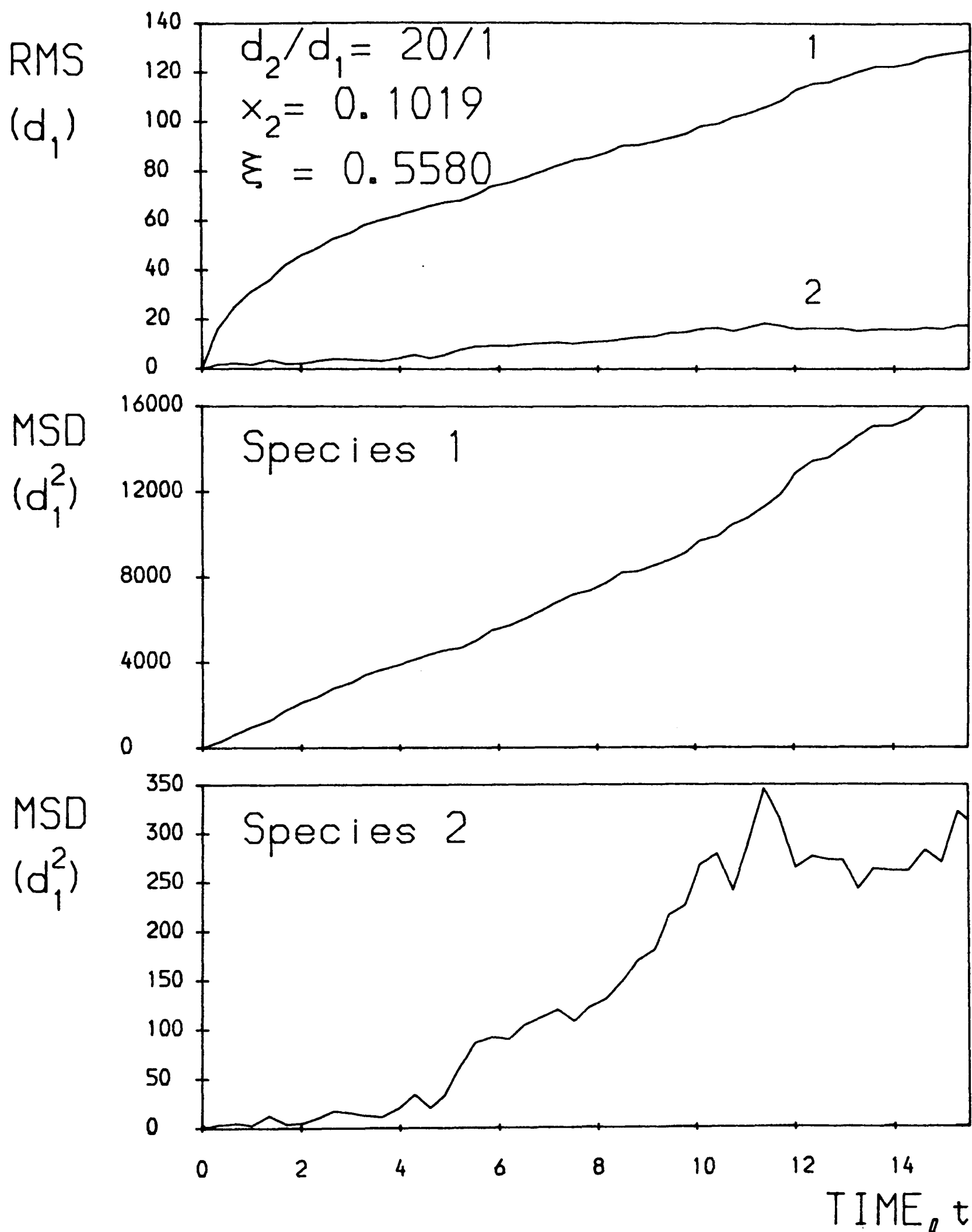


Fig. 2.33 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

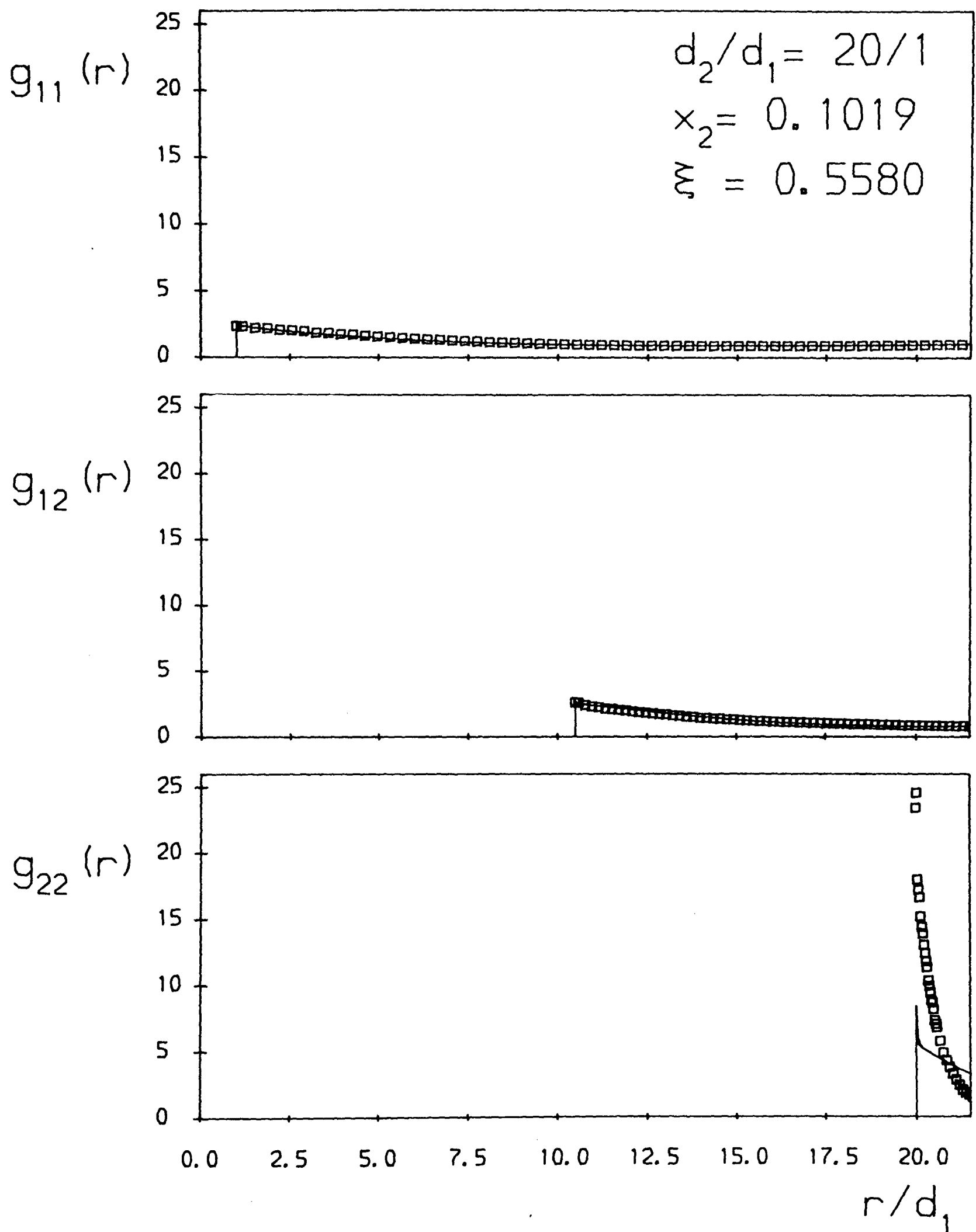


Fig. 2.34 The radial pair distribution functions for binary mixtures of hard spheres.

The values of the radial distribution functions at different separations, in terms of the diameter of the small spheres 1, are shown in Fig. 2.34 for a density of $\xi=0.5580$, and no solid-like structure is seen. The exact contact values of the distribution functions obtained from the molecular dynamics simulations are $g_{11}(d_1)=2.36$, $g_{12}(d_{12})=2.62$, and $g_{22}(d_2)=23.4$ corresponding to a value of the compression factor $Z=7.84$. This result can be compared with the average value of $Z=7.15$ obtained using the virial equation during the simulation. The contact values calculated theoretically using the correction to the Perram method are $g_{11}(d_1)=2.48$, $g_{12}(d_{12})=2.69$, and $g_{22}(d_2)=8.35$ with $Z=4.46$. Hence, the theory underestimates the contact values of the radial distribution function $g_{22}(r)$ and the compression factor for this system. The fact that the Mansoori equation underestimates the compression factor at this mole fraction for high density states is in accordance with these findings. It must be noted that at larger separations the theoretical and exact radial distribution functions are in good agreement.

The equimolar mixture with $d_2/d_1=20/1$ displays a solid transition at a density of $\xi=0.49$. Fig. 2.35 shows that the motion of both species is fluid-like for a density $\xi=0.45$ along the liquid branch of the curve in Fig. 2.12. Above the transition density the large spheres 2 crystallize into a solid lattice while the smaller spheres are free to move in the interstices. The mean-square displacement of the large spheres for a density of $\xi=0.5681$ in Fig. 2.36 shows

non-diffusive motion associated with a solid-like state. The mean-square displacement of species 2 oscillates about an average value for a significant amount of time although at times the spheres move sharply from one lattice site to another presumably due to lattice dislocations. The dislocations in the solid structure seem to arise because the number of large spheres does not conform with the periodic boundary conditions. The transition to the solid phase as the density is increased can be seen in Fig. 2.37 when the diffusion coefficient of component 2 effectively becomes zero.

The radial distribution functions for the $d_2/d_1=20/1$ equimolar mixture are shown for a liquid and a solid state in Fig. 2.38 and Fig. 2.39 respectively. It is clear from Fig. 2.38 representing a liquid density of $\xi=0.45$ that the molecular dynamics results, squares, and the theoretical curve are in good agreement although the $g_{11}(d_1)$ contact value is underestimated by the theory. The contact values of the distribution functions obtained from the computer data are $g_{11}(d_1)=1.92$, $g_{12}(d_{12})=2.08$, and $g_{22}(d_2)=4.58$, whilst the theoretical values are $g_{11}(d_1)=1.93$, $g_{12}(d_{12})=2.04$, and $g_{22}(d_2)=4.67$. The value of the compression factor determined from the theoretically calculated contact values, $Z=5.73$, compares favorably with the value of $Z=5.67$ obtained from the exact contact values, and also with the value of $Z=5.63$ obtained using the virial equation.

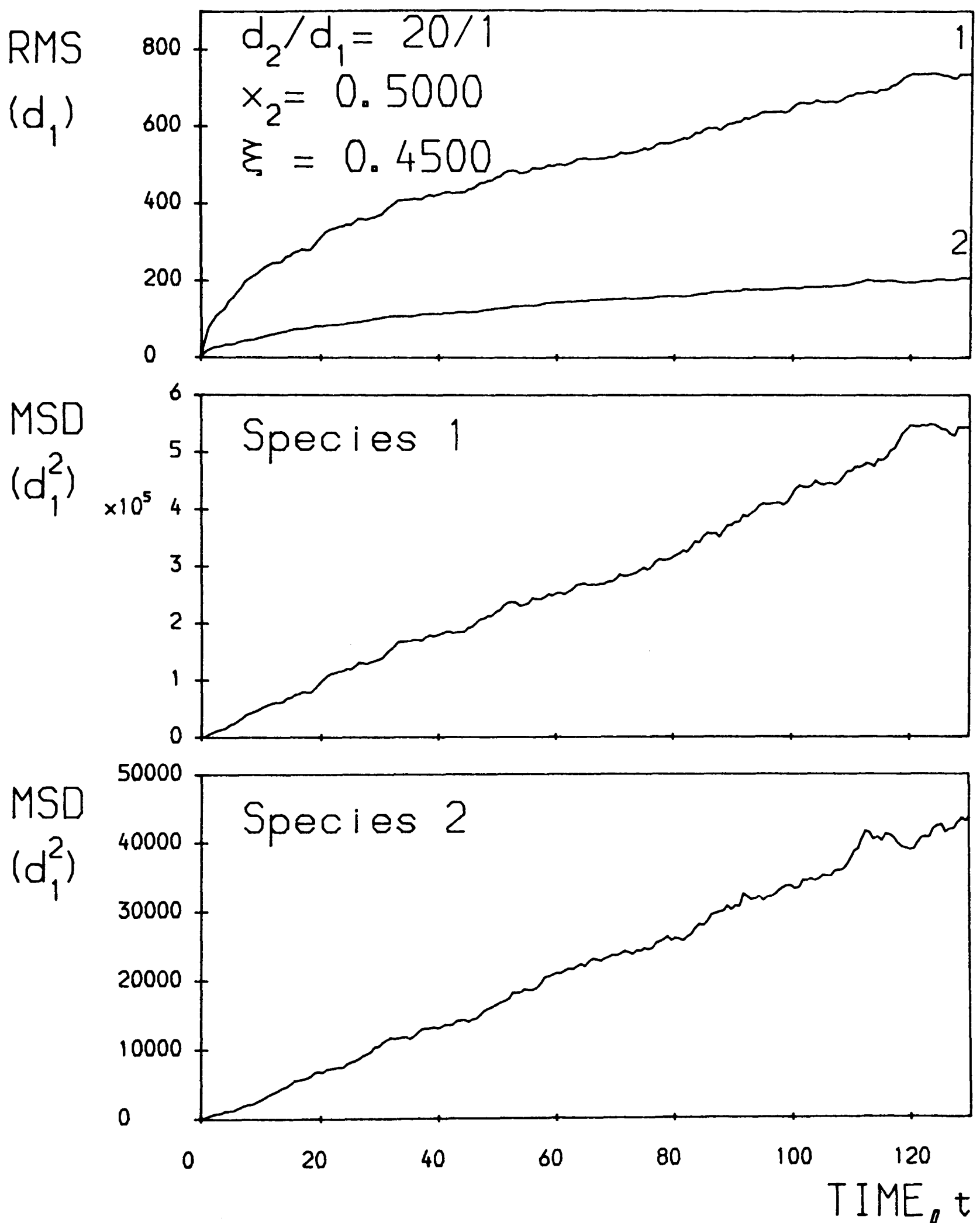


Fig. 2.35 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

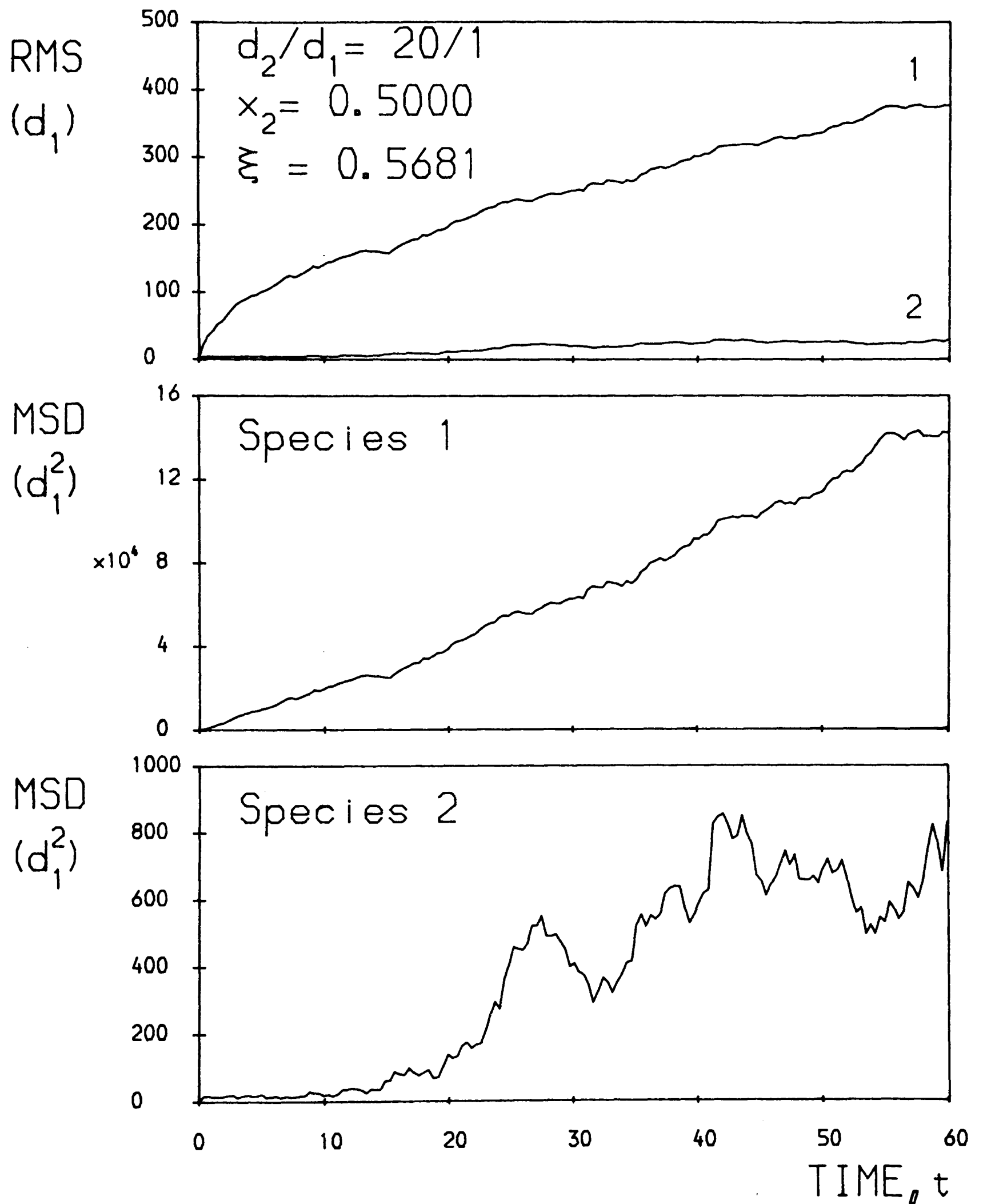


Fig. 2.36 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

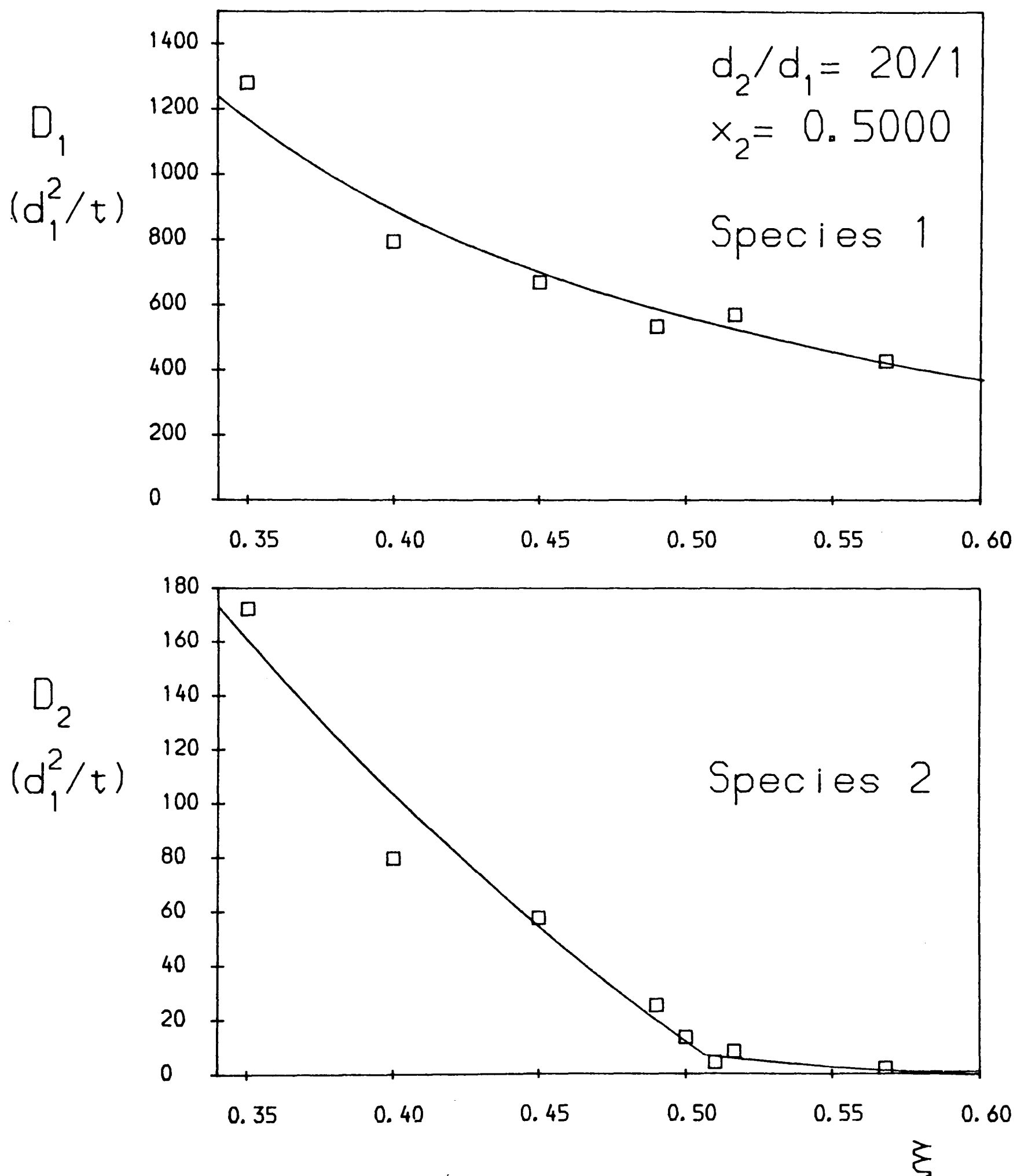


Fig. 2.37 The self-diffusion coefficients of species 1, D_1 , and species 2, D_2 , as a function of density, ξ , for a binary mixture of hard spheres.

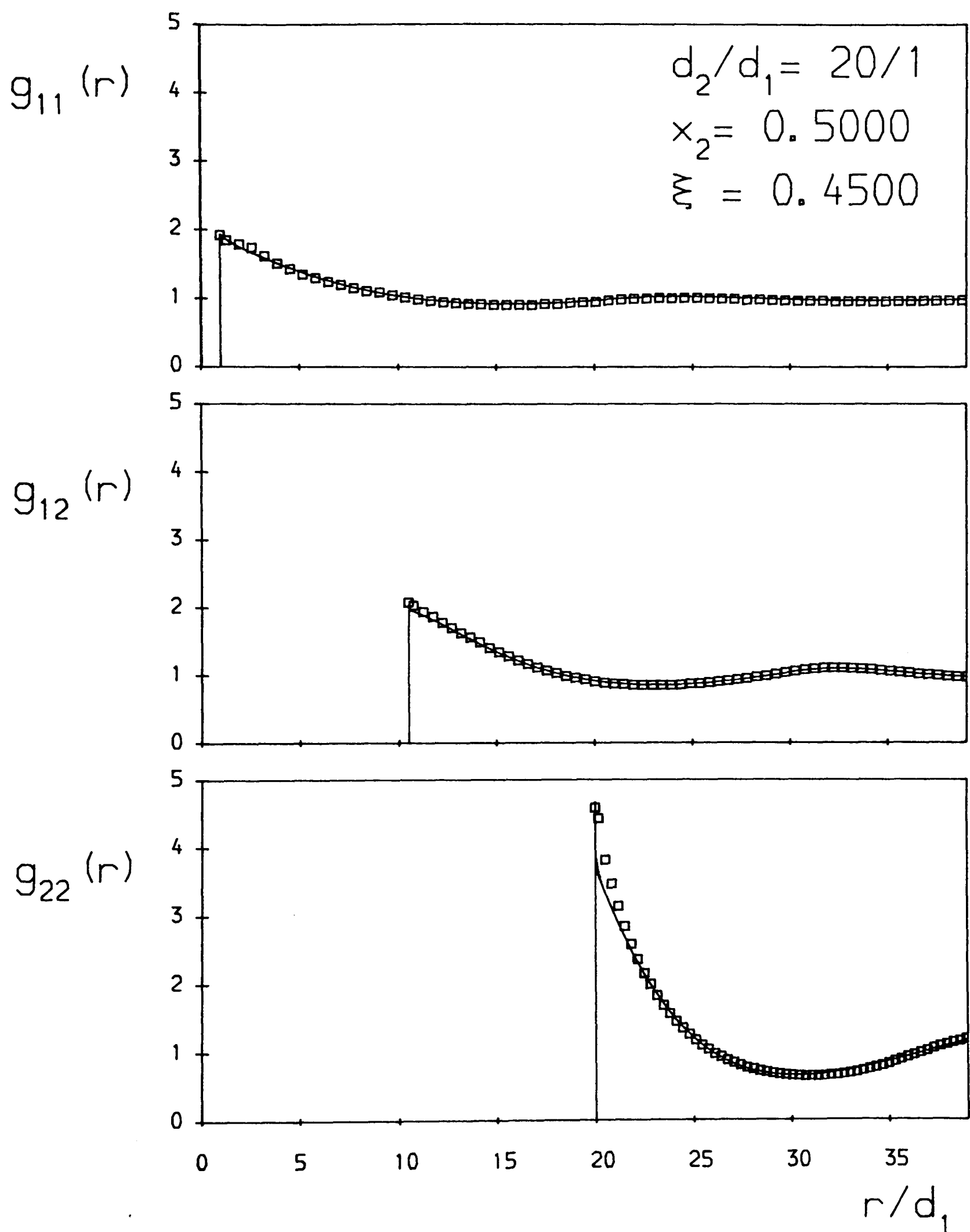


Fig. 2.38 The radial pair distribution functions for binary mixtures of hard spheres.

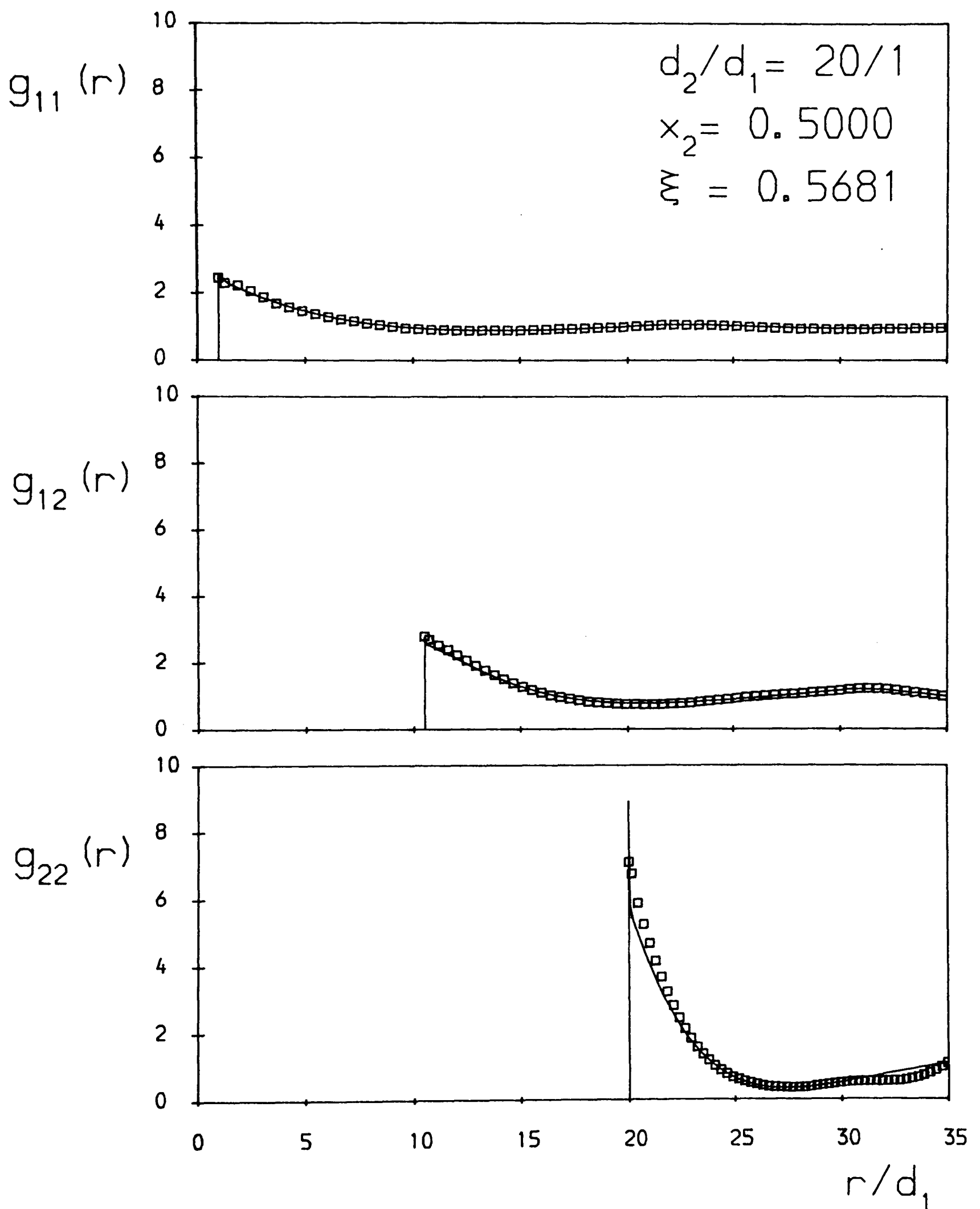


Fig. 2.39 The radial pair distribution functions for binary mixtures of hard spheres.

The distribution functions obtained for a solid density of $\xi=0.5681$ are shown in Fig. 2.39. No solid-like structure is seen with the radial distribution function of the small spheres $g_{11}(r)$ indicating that the solid lattice is made up exclusively of the large spheres 2. Consequently, $g_{22}(r)$ shows a certain solid-like structure which is not predicted by the theoretical curve, but because the simulation was undertaken for a relatively small system, the curve cannot be extended to the larger separations where more structure is expected. The contact values obtained from the simulations are $g_{11}(d_1)=2.46$, $g_{12}(d_{12})=2.80$, and $g_{22}(d_2)=7.09$, and the contact values determined from theory are $g_{11}(d_1)=2.55$, $g_{12}(d_{12})=2.77$, and $g_{22}(d_2)=8.91$. The Percus-Yevick theory is seen to overestimate the contact values of $g_{11}(d_1)$ and $g_{22}(d_2)$, consequently the theoretical value of the compression factor $Z=12.0$ is larger the value of $Z=9.98$ calculated from the exact contact values, whilst the virial result is $Z=9.95$.

The hard sphere mixture with $d_2/d_1=20/1$ and $x_2=0.8981$ also shows a phase transition to a solid, but it occurs at the higher density of about $\xi=0.53$. Fig. 2.40 for a liquid density of $\xi=0.45$ and Fig. 2.41 for a solid density of $\xi=0.5651$ display the root-mean-square and mean-square displacements for each species as a function of time. The diffusion coefficients calculated from the slopes of the mean-square displacements at different densities are shown in Fig. 2.42. As expected there is a discontinuous change in the motion of the large spheres 2 at the solid transition

when the diffusion coefficient becomes zero. The small spheres 1 remain relatively mobile at high densities.

The radial distribution functions for the system with $d_2/d_1=20/1$ and $x_2=0.8981$ at a liquid and a solid density are shown in Fig. 2.43 and Fig. 2.44. Fig. 2.43 corresponds to a density of $\xi=0.45$ along the liquid branch of the curve in Fig. 2.13. The Percus-Yevick results are in good agreement with the exact results. The theoretically calculated contact values of the distribution functions are $g_{11}(d_1)=1.93$, $g_{12}(d_{12})=2.04$, and $g_{22}(d_2)=4.73$, and the corresponding value of the compression factor is $Z=8.75$. The exact results obtained from molecular dynamics are $g_{11}(d_1)=1.18$, $g_{12}(d_{12})=2.05$, and $g_{22}(d_2)=4.59$ with $Z=8.54$. These results are in good agreement with the value of $Z=8.66$ obtained from the virial equation. It appears that the theory overestimates the contact value of $g_{11}(d_1)$, although the statistical error is considerable due to the small number of particles of species 1 used in the simulation. Nevertheless, the agreement between the theoretical curve and the exact results is good for this density.

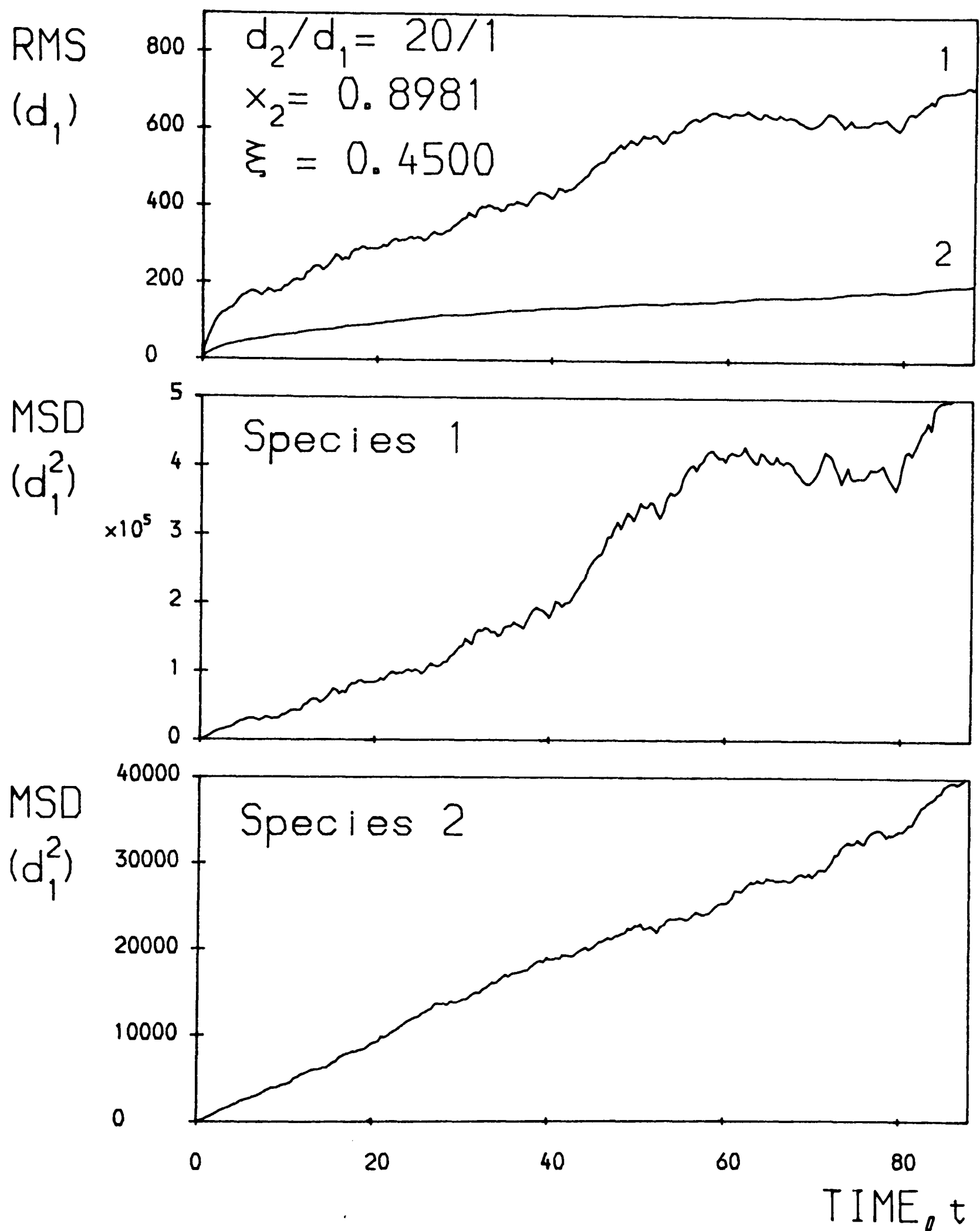


Fig. 2.40 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

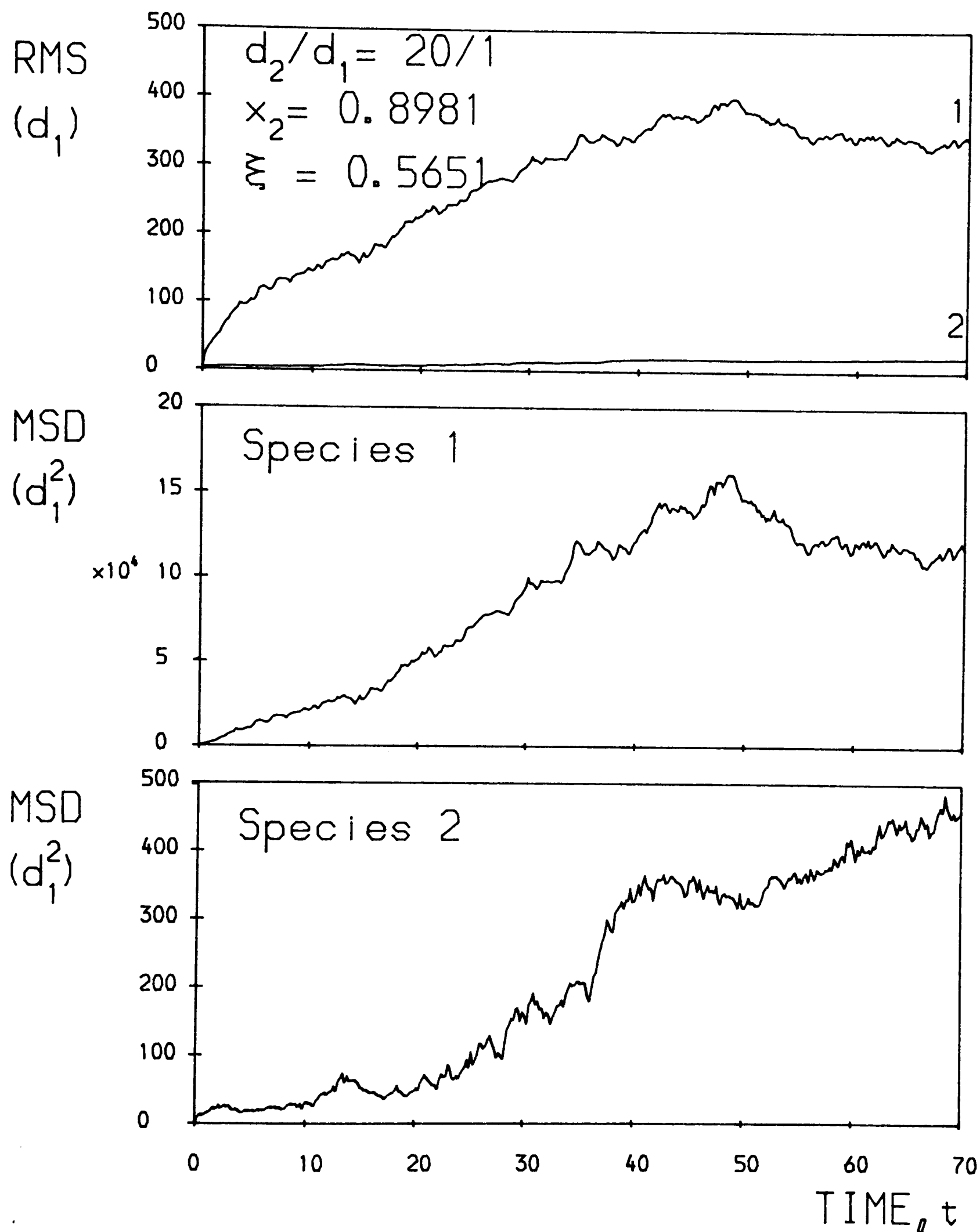


Fig. 2.41 The root-mean-square displacement RMS and mean-square displacement MSD for each species of a binary hard sphere mixture.

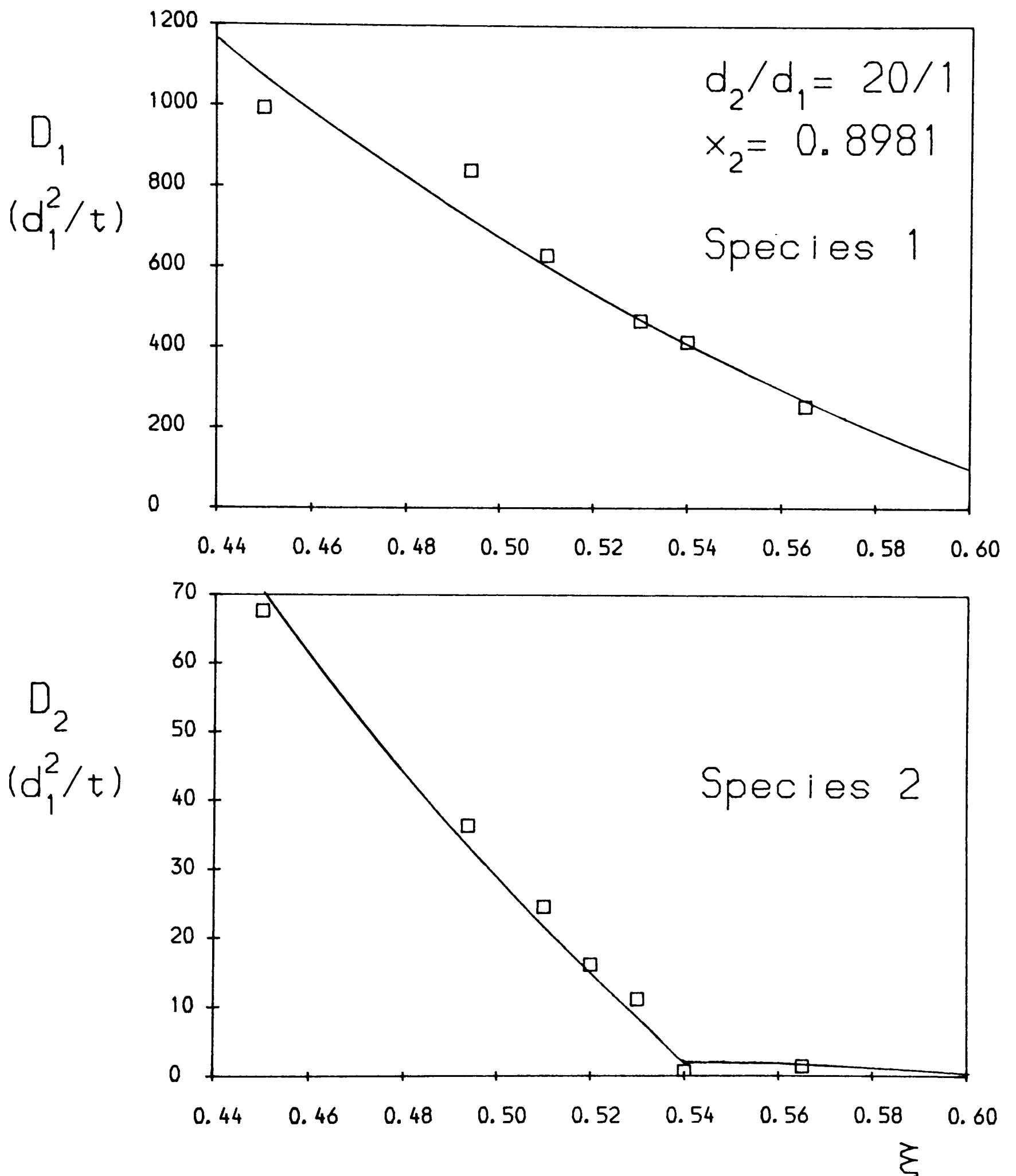


Fig. 2.42 The self-diffusion coefficients of species 1, D_1 , and species 2, D_2 , as a function of density, ξ , for a binary mixture of hard spheres.

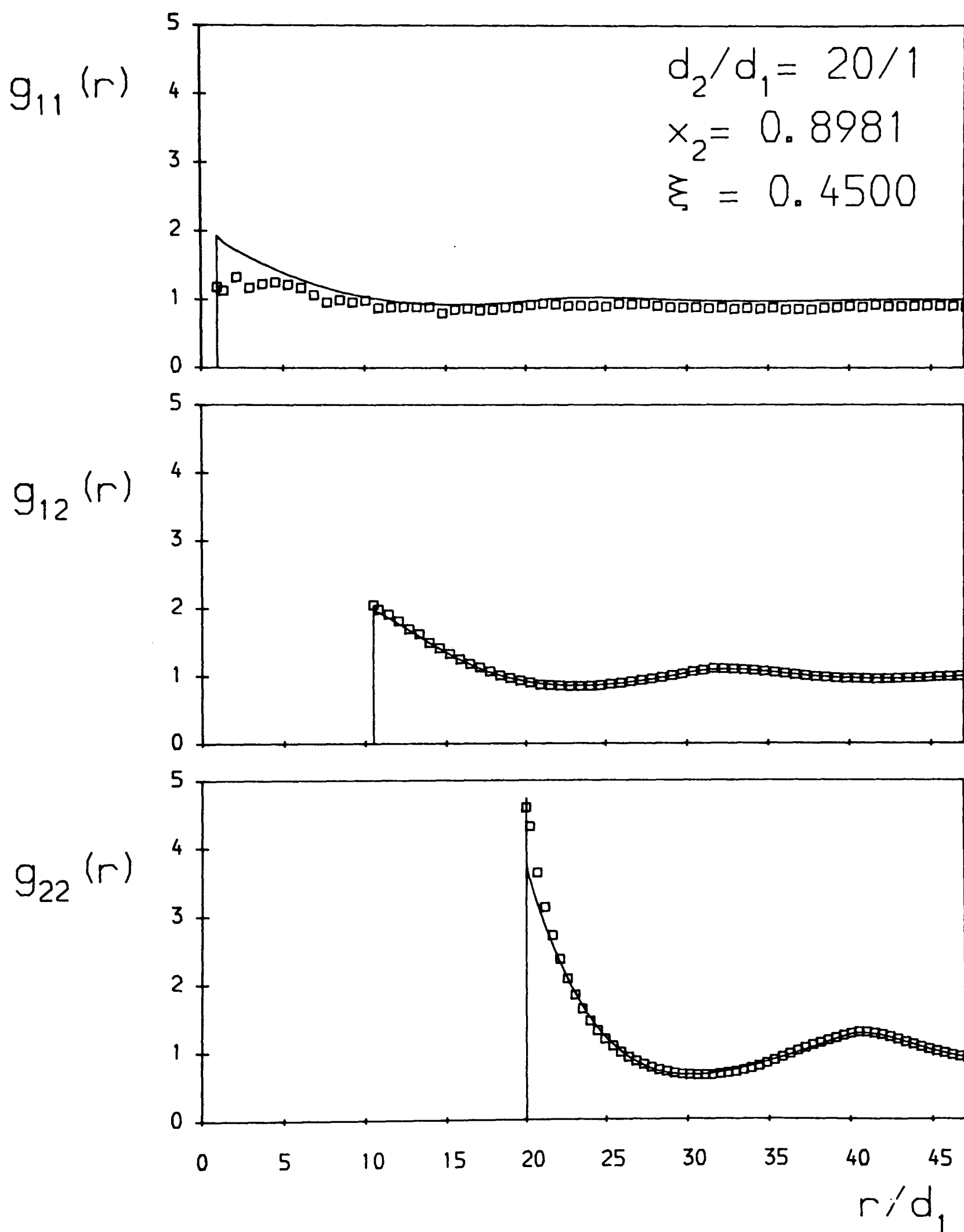


Fig. 2.43 The radial pair distribution functions for binary mixtures of hard spheres.

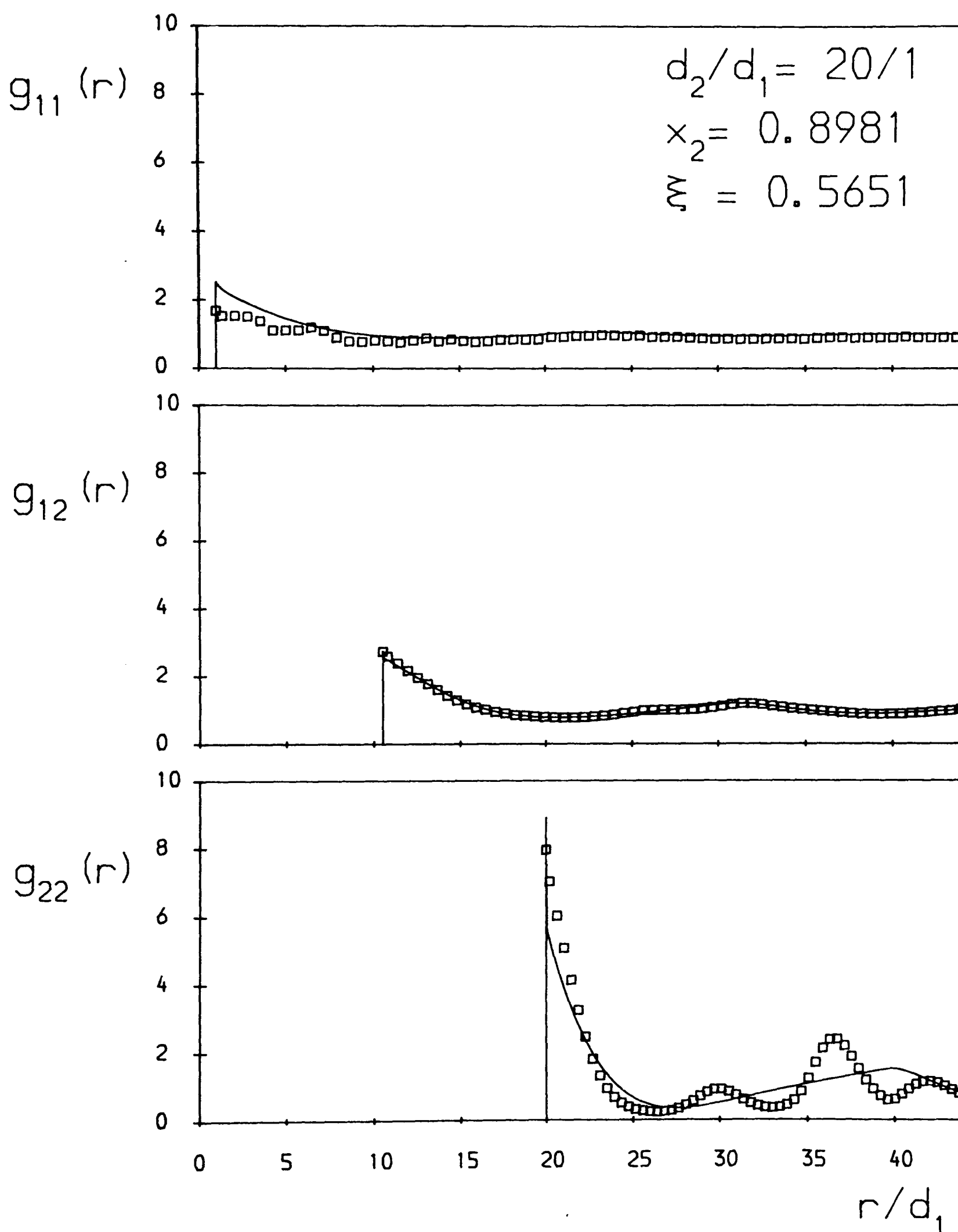


Fig. 2.44 The radial pair distribution functions for binary mixtures of hard spheres.

The agreement is not so good for a solid density of $\xi=0.5651$ as shown in Fig. 2.44. The radial distribution function of the large spheres $g_{22}(r)$ has gained a great deal of structure characteristic of a solid phase, which is not predicted by the Percus-Yevick theory. The characteristic peaks appearing in the curve of $g_{22}(r)$ at separations $r/d_1=29$ and $r/d_1=36$ represent the first- and second-nearest neighbours of a face-centred cubic lattice [35]. The theoretical results of $g_{11}(d_1)=2.53$, $g_{12}(d_{12})=2.75$, $g_{22}(d_2)=8.90$ and $Z=19.3$ are poor representations of the exact values of $g_{11}(d_1)=1.75$, $g_{12}(d_{12})=2.78$, $g_{22}(d_2)=7.94$ and $Z=17.3$, with $Z=16.4$ calculated from the virial equation.

It is clear from this analysis that the Percus-Yevick theory and hence the Mansoori equation is a good representation of a binary hard sphere mixture's properties along the fluid branch of the equation of state even when the two spheres are very different in size. The Mansoori equation fails beyond the solid transition by overestimating the value of the compression factor along the solid branch of the equation of state.

2.4.2.5 Discussion -

The values of the total reduced density ξ at which a transition from a liquid to a solid phase was seen are summarized in the table below for the various binary hard sphere mixtures investigated.

x₂ d₂/d₁	0.0	0.0648	0.1019	0.5000	0.8981	1.0
1	0.49	0.49	0.49	0.49	0.49	0.49
11/10	0.49			0.49		0.49
5/3	0.49				0.52	0.49
3/1	0.49				0.53	0.49
5/1	0.49			0.52	0.53	0.49
20/1	0.49			0.49	0.53	0.49

As discussed in Section 2.3 the transition from a liquid phase to a solid phase in an assembly of pure hard spheres occurs at about $\eta=0.49$. In the binary mixtures of hard spheres investigated solid transitions also take place although the densities at which they occur depend quite critically on the magnitude of the size ratio and the composition. When the size difference is small as with the system $d_2/d_1=11/10$ studied by Rotenberg, the transition density is about $\xi=0.49$ as for the pure system. However, the problem is much more complicated when the spheres vary significantly in size.

For binary mixtures with diameter ratios of $d_2/d_1=5/3$ and $d_2/d_1=3/1$ it seems that the mixtures find it difficult to solidify because the smaller spheres cannot be

accommodated in the spaces of a lattice formed by the larger spheres, and complex lattices will have to be formed. For a tetrahedral arrangement of the large spheres the critical value of the diameter ratio that allows the large spheres to touch with a small sphere in between them can be calculated using straight-forward geometry to be $d_2/d_1=4.45$. Hence, in the case of systems with size ratios $d_2/d_1 < 4.45$ lattice formation may be quite difficult, as seen for the equimolar mixtures with $d_2/d_1=5/3$ and $d_2/d_1=3/1$ which do not seem to exhibit a transition to the solid at the densities studied. These systems will form a lattice when the proportion of the large spheres approaches the pure hard sphere value with mole fractions of $x_2=0.8981$. The small and large spheres eventually solidify into a lattice when the density is increased at these mole fractions.

For the binary hard sphere mixtures with $d_2/d_1 > 4.45$ such as $d_2/d_1=5/1$ and $d_2/d_1=20/1$, the larger spheres can form a lattice with the smaller spheres moving freely in the resulting spaces. Consequently, these mixtures enable the solid transition to occur more easily, and solid phases are observed with equimolar mixtures when the size ratio is $d_2/d_1=5/1$ and $d_2/d_1=20/1$. However, it must be noted that when the proportion of the larger spheres in the mixture is small as with a mole fraction of $X_2=0.1019$, the formation of a solid lattice remains difficult and no solid transition is seen.

Ermak et al. [42] have reported molecular dynamics simulation results for hard sphere solids with one smaller

fluid component, in order to find the largest spheres that can be introduced at every equivalent interstitial site of a given crystal structure without melting the whole crystal. Their calculations of the diffusion coefficients show that a diameter ratio no smaller than $d_2/d_1=2.5$ can be achieved in a face-centred cubic crystal without both components becoming either localized or fluid. Clearly these findings are consistent with the results presented in the previous sections. The density-functional theory of freezing has also been extended to investigate the crystallization of binary hard sphere mixtures by Barrat et al. [43]. Systems with diameter ratios in the range $1 < d_2/d_1 < 1.18$ were found to have complex liquid-solid phase diagrams. For $d_2/d_1 > 1.18$, Barrat et al. found that it becomes increasingly difficult to find a mechanically stable solid phase for a gradually increasing range of intermediate concentrations. However, at a critical value of d_2/d_1 it will be possible for the larger spheres to form a lattice which can accommodate the smaller spheres.

A word of caution is necessary at this point. All the simulations presented in this chapter were performed for systems of 108 particles in a cubic box with the use of periodic boundary conditions. In the case of a face-centred cubic lattice, the numbers of particles that are required to form an infinitely repeating lattice are 4, 32, 108, 256, or the series with $4n^3$. Clearly, when the number of particles in the system does not comply with the requirements imposed by the periodic boundary conditions, it may be impossible to

form an infinite crystal lattice and dislocations will occur. This might have an effect on the value of the transition density determined from the simulation data. Because some of the mixtures of hard spheres investigated will attempt to solidify into complex lattices at higher densities, it may be difficult for a solid lattice to form under the prescribed conditions. In certain cases a thermodynamically stable solid lattice may fail to form altogether during the course of the simulation.

Further simulations of mixtures of hard spheres are required at this stage to check the results presented in this section. A more detailed study of the solid transition in these mixtures is planned for larger systems in a periodic box which can fluctuate in shape as well as in volume.

2.5 CONCLUSION

In this chapter we have seen that the isothermal-isobaric NPT Monte Carlo method is comparable in accuracy to the molecular dynamics technique for calculating the thermodynamic properties of binary hard sphere mixtures. The Monte Carlo simulations adequately sample phase space and the ergodic hypothesis appears to hold true even at very high densities. An advantage of the molecular dynamics method is that it provides dynamical information which can be analysed to probe the system's state. However, high density configurations of different-sized spheres are

difficult to obtain with conventional molecular dynamics simulations. The constant-pressure NPT Monte Carlo method easily solves this problem by providing high density hard sphere configurations which can be used to start off the molecular dynamics simulations. The combined use of isothermal-isobaric Monte Carlo and molecular dynamics simulations proved to be a powerful tool in investigating the properties of hard sphere mixtures.

The Mansoori equation of state has been thoroughly checked in this chapter, and it is found to be an accurate representation of the properties of binary hard sphere mixtures. A good agreement between the Mansoori and exact equations of state is seen along the liquid branch of the curve up to the solid transition. Above the solid transition, the Mansoori equation overestimates the value of the compression factor. These observations hold even when the two spheres are very different in size as shown for a binary hard sphere mixture with a diameter ratio of $d_2/d_1=20/1$. In this case the Mansoori equation accurately describes the hard sphere properties for the fluid densities, although small negative deviations from the exact result are seen for low mole fractions of the larger spheres. Thus, the use of the Mansoori equation in Chapters 4 and 5 to determine the fluid phase equilibria of hard core mixtures with one component much larger than the other is justified.

The transition from the fluid phase to the solid phase has also been investigated in Section 2.4.2 for various

binary mixtures of hard spheres. This preliminary study has yielded some very interesting results. Systems with diameter ratios $d_2/d_1=5/3$ and $d_2/d_1=3/1$ find it difficult to solidify at higher densities, although some complex lattices form at high mole fractions of the large spheres. When the size ratio is $d_2/d_1=5/1$ or $d_2/d_1=20/1$, the large spheres freeze into solid lattices quite easily with the small spheres moving in the interstices. A more thorough study is required at this stage.

The results of the constant-pressure Monte Carlo and molecular dynamics simulations of binary hard sphere mixtures of different sizes and compositions are summarized in Appendix I and Appendix II respectively.

CHAPTER 3

PURE HARD CORES

3.1 AUGMENTED VAN DER WAALS EQUATION

The Carnahan-Starling equation [6] introduced in Chapter 1 does not exhibit gas-liquid phase transitions because it represents a system of hard sphere molecules with repulsive cores. Since the hard sphere equation cannot be used on its own for any gas-liquid equilibrium calculations, a van der Waals attractive term, $-a/V^2$ (internal pressure), is added as a perturbation to the accurate hard sphere relation. The resulting equation of state accurately describes a system of hard spheres between which there are weak but long-ranged attractive interactions [44],[45],[46]. This hard core fluid displays a region of gas-liquid phase coexistence which ends at a classical critical point. The pressure of the pure hard core system is expressed in terms of the reduced density η by using the Carnahan-Starling expression for the compressibility:

$$P = \frac{\eta(1+\eta+\eta^2-\eta^3)RT}{b(1-\eta)^3} - \frac{a\eta^2}{b^2}$$

$$b = \frac{\pi L d^3}{6}, \quad \eta = \frac{b}{V_m}$$

In effect, the repulsive term of van der Waals's famous equation has been replaced by the accurate hard sphere term obtained by Carnahan and Starling to give an "augmented van der Waals" equation of state [47]. The equation's properties are similar to those of the van der Waals equation which implies gas-liquid coexistence when the attractive forces are about equal to the repulsive forces.

3.2 THE CRITICAL POINT

The position of the critical point for the pure hard core equation of state can be determined by examining the first and second derivatives of the pressure with respect to volume at constant temperature. The conditions for the gas-liquid critical point in a one-component system are

$$\left(\frac{\partial P}{\partial V} \right)_T = 0 \quad , \quad \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0$$

For the Carnahan-Starling equation the corresponding derivatives can be expressed as

$$\begin{aligned} \left(\frac{\partial P}{\partial V} \right)_T &= \frac{\eta_c^2}{b^2} \frac{(-1-4\eta_c-4\eta_c^2+4\eta_c^3-\eta_c^4)}{(1-\eta_c)^4} RT_c + \frac{2a\eta_c^3}{b^3} = 0 \\ \left(\frac{\partial^2 P}{\partial V^2} \right)_T &= \frac{\eta_c^3}{b^3} \frac{(2+14\eta_c+20\eta_c^2-20\eta_c^3+10\eta_c^4-2\eta_c^5)}{(1-\eta_c)^5} RT_c \\ &\quad - \frac{6a\eta_c^4}{b^4} = 0 \end{aligned}$$

The two equations are solved simultaneously for the reduced critical density η_c by eliminating the two constants, a and b , together with the temperature as the factor a/bRT_c . A fifth order polynomial is obtained

$$\eta_c^5 - 5\eta_c^4 + 4\eta_c^3 + 20\eta_c^2 + 5\eta_c - 1 = 0$$

which is solved numerically for the critical density with a positive root at

$$\eta_c = 0.130444$$

An expression for the critical temperature T_c in terms of the constants a and b can be obtained by resubstituting this value of the reduced critical density in either of the two derivatives. In the case of the first derivative the expression is

$$A_c = \frac{a}{bRT_c} = \frac{(1+4\eta_c+4\eta_c^2-4\eta_c^3+\eta_c^4)}{2\eta_c(1-\eta_c)^4} = 10.6012$$

The critical pressure P_c is related to the constants and the reduced critical density in the following way

$$\frac{P_c b^2}{a} = \eta_c^2 \frac{(1-4\eta_c-4\eta_c^2+\eta_c^4)}{(1+4\eta_c+4\eta_c^2-4\eta_c^3+\eta_c^4)} = 4.41681 \times 10^{-3}$$

and this expression together with A_c allows us to determine the compression at the critical point

$$Z_c = \frac{P_c V_c}{NkT_c} = \frac{(1-4\eta_c-4\eta_c^2+\eta_c^4)}{2(1-\eta_c)^4} = 0.358956$$

It is instructive to compare these values of the critical constants with those obtained using the van der Waals equation. The two equations are compared in terms of the previously defined b parameter as shown below.

	van der Waals	Carnahan-Starling
η_c	$1/12 = 0.0833333$	0.130444
A_c	13.5	10.6012
Z_c	$3/8 = 0.375$	0.358956

The value of $Z_c=0.359$ obtained for the critical compression is still higher than experimentally calculated values (eg. argon has a critical compression of $Z_c=0.291$). However, the Carnahan-Starling result is clearly better than the van der Waals result of $Z_c=0.375$. A more detailed comparison of each system's gas-liquid phase equilibria is achieved by determining the vapour pressure curve for the hard core system and comparing it with the corresponding van der Waals curve.

3.3 THE ISOTHERMS

Once the critical constants are known, the hard core equation of state can be expressed in terms of the reduced pressure, temperature and density. The reduced form of the equation is

$$P_r = \frac{\eta(1+\eta+\eta^2-\eta^3)T_r}{\eta_c Z_c (1-\eta)^3} - \frac{A_c \eta^2}{\eta_c Z_c}$$

where

$$P_r = P/P_c, \quad T_r = T/T_c$$

$$\eta_c = 0.130444, \quad A_c = 10.6012, \quad Z_c = 0.358956$$

Fig. 3.1 shows the pressure-volume-temperature, PVT, surface calculated from the hard core expression. Various of the equation's isotherms are also plotted at the critical temperature and at temperatures just above and below the critical point. Reduced pressure versus reduced molar volume curves are shown with the pressure becoming infinite as the reduced density approaches the value of $\eta=1.0$ in excess of the close-packing value of $\eta=0.74$. This feature can clearly be seen in the corresponding PVT surface which shows steep slopes corresponding to large changes in pressure at low reduced volumes.

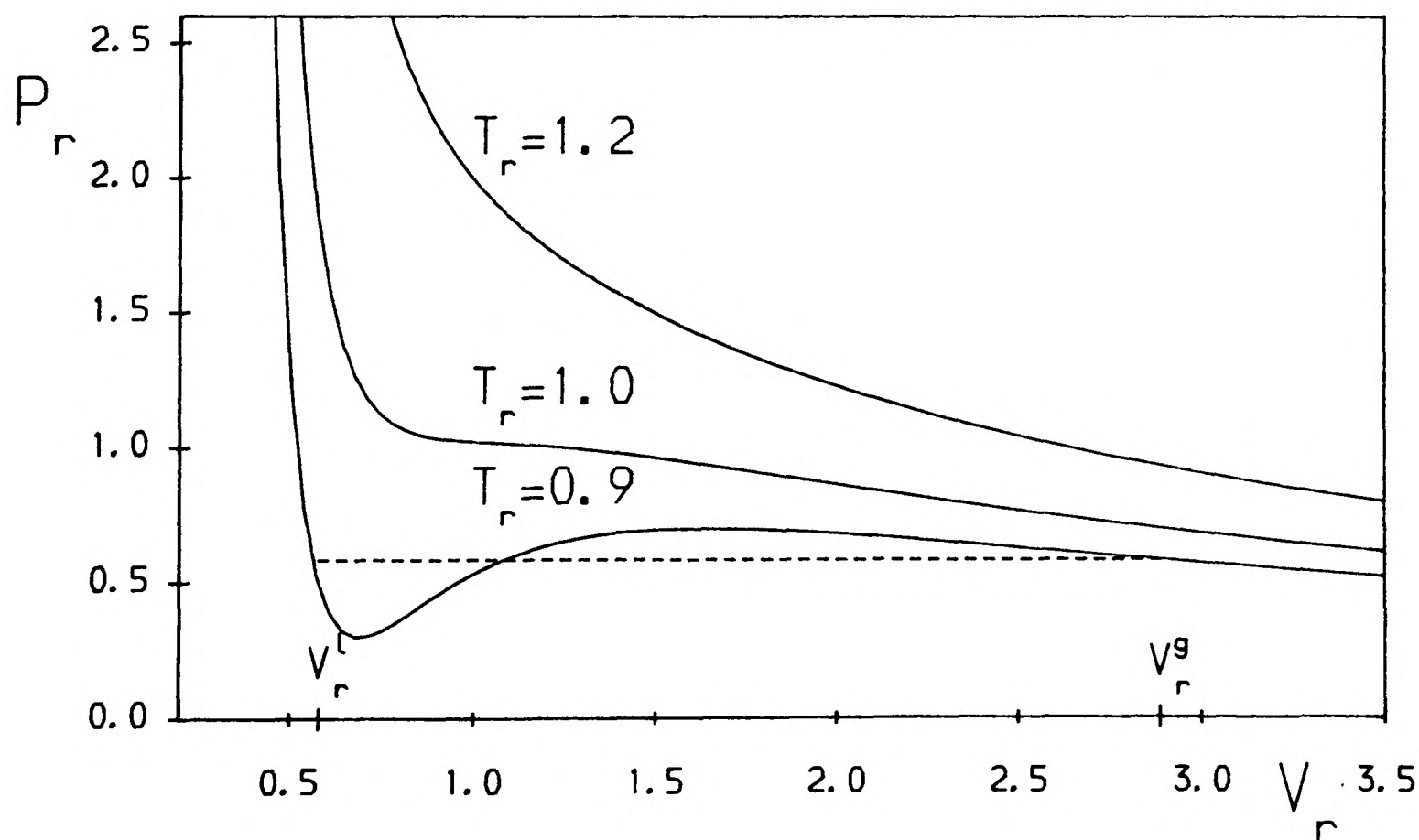
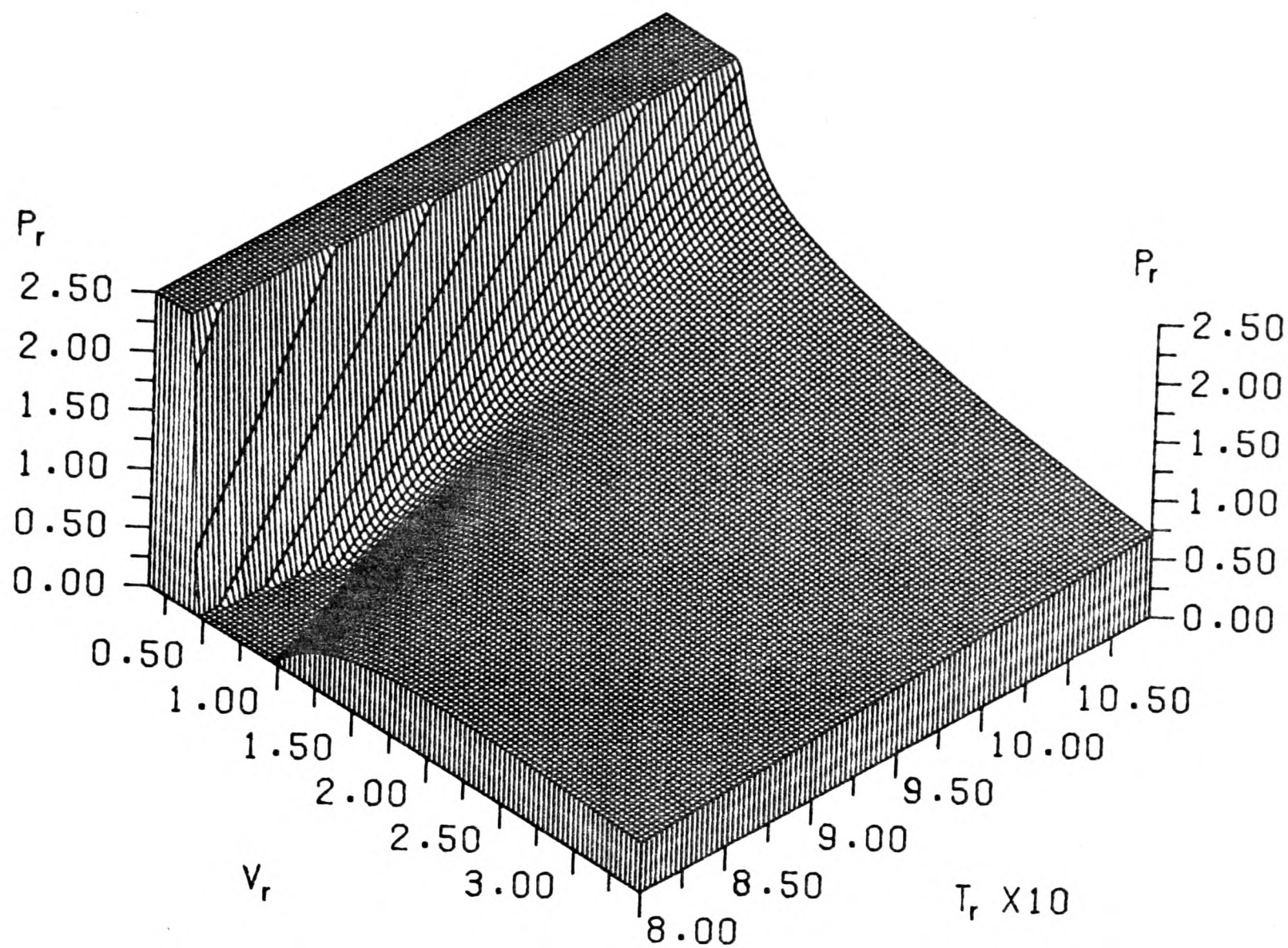


Fig. 3.1 The Carnahan-Starling PVT surface and isotherms.

3.4 THE VAPOUR PRESSURE CURVE

The oscillating portions of the isotherms, which also include metastable and unstable states, can be identified with the region where gas and liquid coexist. The equal area construction introduced by Maxwell is shown on Fig. 3.1 as the dashed line joining the molar volumes of gas, v_r^g , and liquid, v_r^l , in equilibrium. For liquid and vapour to coexist the two phases must be at the same temperature, pressure and chemical potential.

Thus the conditions for equilibrium are

$$P_g = P_l, \quad T_g = T_l, \quad \mu_g = \mu_l$$

and the equal area construction follows from the fact that the isotherm's integral over the liquid and gas volumes must be zero

$$\mu_g = \mu_l, \quad \int_l^g v \left(\frac{\partial P}{\partial v} \right)_T dv = 0$$

By applying these conditions to the hard sphere equation, its corresponding gas-liquid equilibrium can be examined. The equation representing the equality of chemical potential is simply

$$\int_l^g v_r \left(\frac{\partial P_r}{\partial v_r} \right)_{T_r} dv_r = \frac{T_r}{Z_c} \left[\ln(\eta/\eta_c) + \frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3} \right]_l^g - \left[\frac{2A_c\eta}{Z_c} \right]_l^g = 0$$

The reduced temperature can be eliminated from this expression, together with the factor a/bRT , by enforcing the condition of equal pressures, representing mechanical equilibrium. After a lengthy algebraic manipulation, a polynomial equation for the reduced density of the gas phase is obtained defined in terms of the parameter r which is the ratio of the reduced densities for the liquid and gas phases in equilibrium.

$$\begin{aligned}
 & [2r^3 - 2r^4 + r^3(r+1) \ln(r)] \eta_g^6 \\
 & + [6r^4 - 6r^2 - (3r^3 + 3r^2)(r+1) \ln(r)] \eta_g^5 \\
 & + [7r - 7r^4 + 9r^2 - 9r^3 + (3r^3 + 9r^2 + 3r)(r+1) \ln(r)] \eta_g^4 \\
 & + [10r^3 - 10r + 5r^4 - 5 - (r^3 + 9r^2 + 9r + 1)(r+1) \ln(r)] \eta_g^3 \\
 & + [3r^2 - 3r + 11 - 11r^3 + (3r^2 + 9r + 3)(r+1) \ln(r)] \eta_g^2 \\
 & + [6r^2 - 6 - (3r + 3)(r+1) \ln(r)] \eta_g \\
 & + [2 - 2r + (r+1) \ln(r)] = 0 \qquad r = \eta_l / \eta_g
 \end{aligned}$$

The saturated vapour density at an arbitrary value of the ratio r can be obtained as a root to the polynomial equation. The equation was solved numerically using a programmable calculator by the method of False Position, examining where the function changes sign. Thus, the saturated vapour and liquid reduced densities are found for a given value of their ratio. Furthermore, the temperature and pressure of phase coexistence are determined by substituting the values obtained for the densities of the two coexisting phases into the equation of state. Since the

gas and liquid phases in equilibrium are at the same temperature and pressure, the two resulting simultaneous equations can be solved to give the vapour pressure and temperature for the corresponding ratio of the densities. By varying this ratio r from the value of one at the critical point to larger values along the coexistence curve, the full vapour pressure curve for the Carnahan-Starling equation is determined (Fig. 3.2).

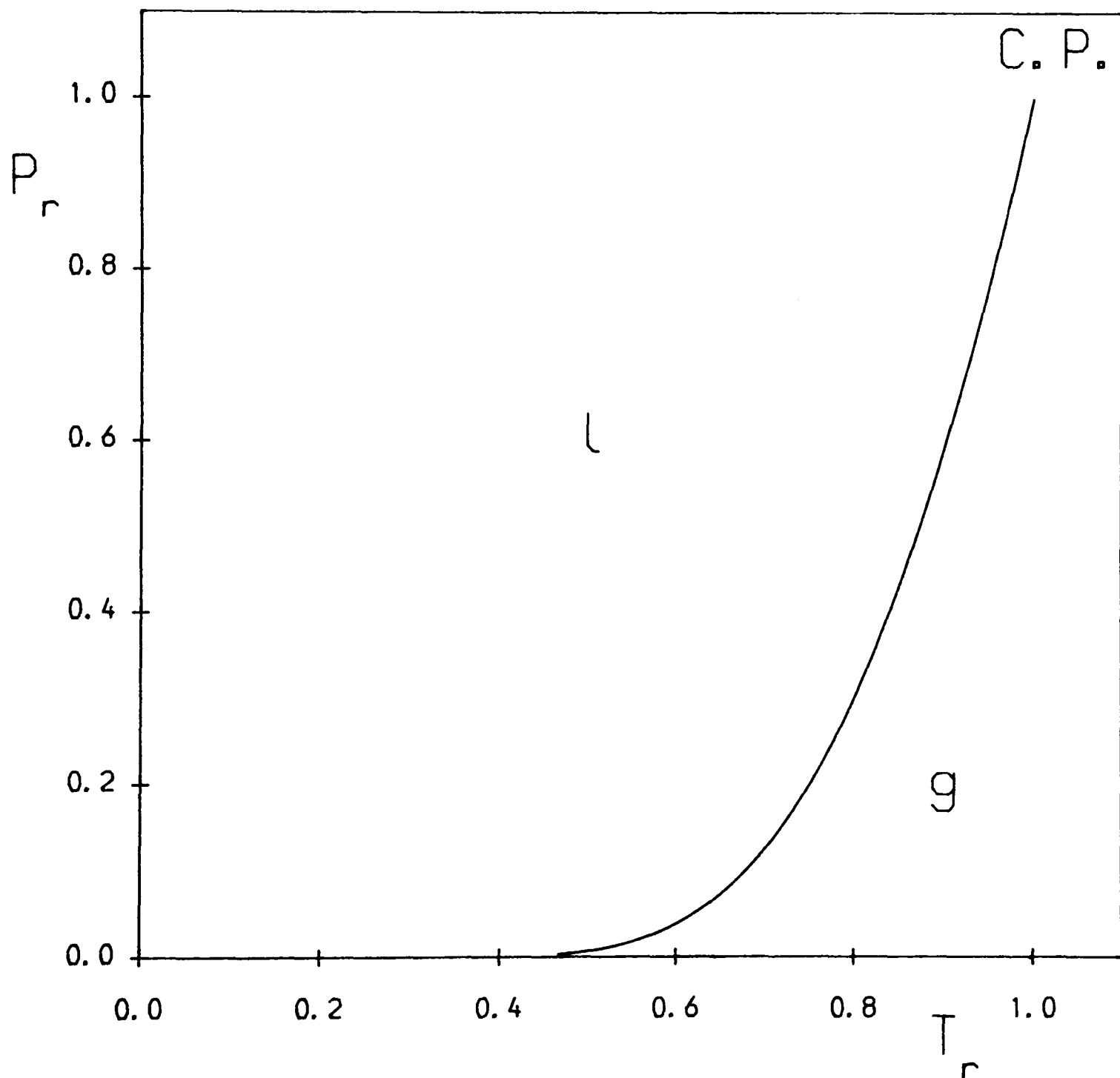


Fig. 3.2 The Carnahan-Starling hard core vapour pressure curve. The critical point is denoted C.P.

The solid curve in Fig. 3.3 shows the coexistence curve obtained for the Carnahan-Starling pure hard core system. These results are in fairly good agreement with the molecular dynamics data of Nicolas et al. [48] for a pure Lennard-Jones fluid, although the hard core equation underestimates the value of the reduced critical density. Appendix III summarizes the Carnahan-Starling results for the vapour pressure curve of the pure hard cores.

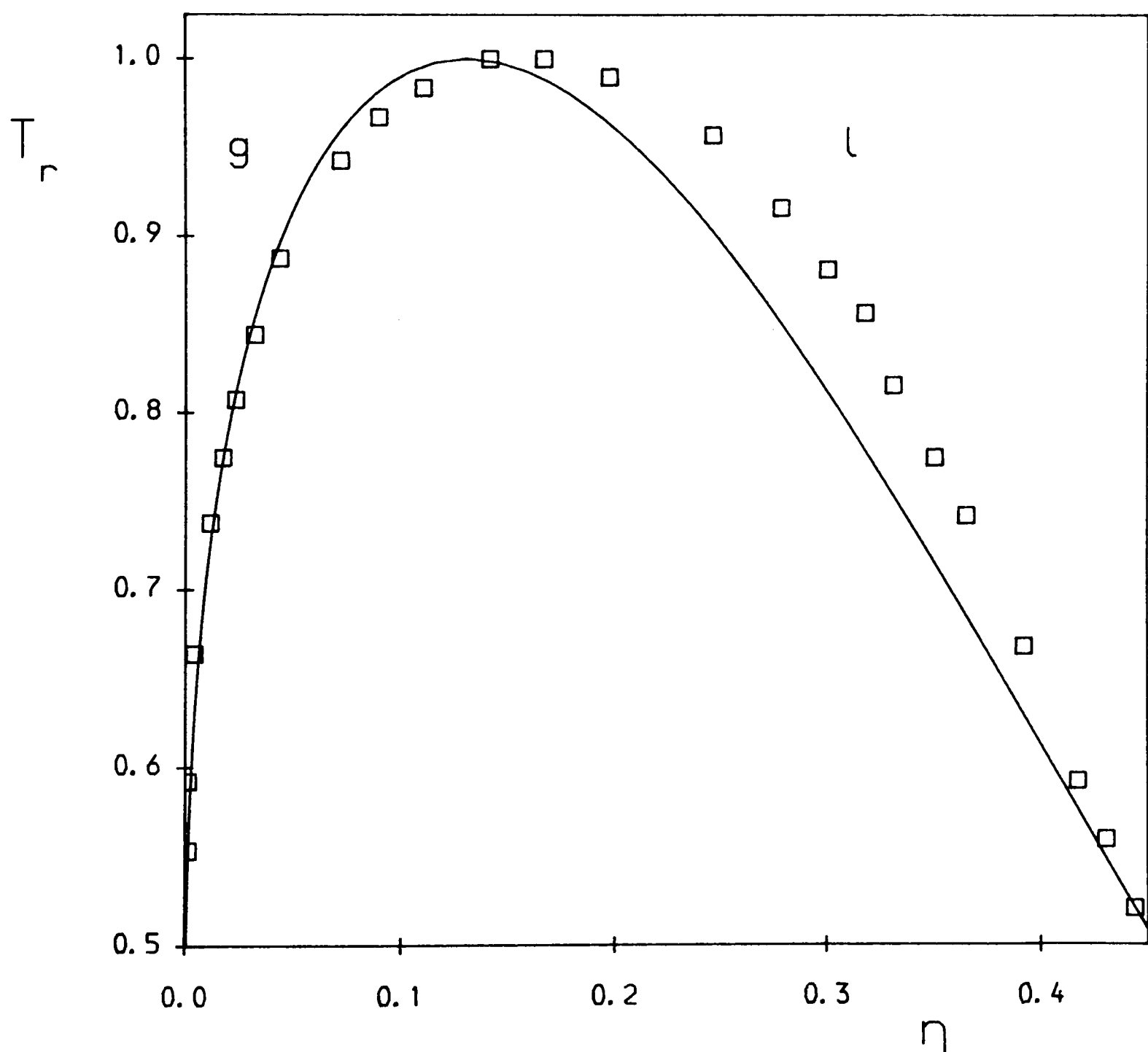


Fig. 3.3 The Carnahan-Starling hard core coexistence curve. The squares represent molecular dynamics data for a Lennard-Jones fluid.

The Carnahan-Starling results are compared with their van der Waals counterparts as well as with the data obtained experimentally for argon by plotting the logarithm of the vapour pressure versus the reciprocal of the temperature (Fig. 3.4); the values for argon are quoted from Rowlinson and Swinton [49], whilst the vapour pressure curve for the van der Waals equation can be obtained via Gibbs's parametric solution [50].

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

$$\chi_l = \frac{(r+1) \ln(r) - 2(r-1)}{r^2 - 2r \ln(r) - 1}, \quad \chi_g = r\chi_l$$

$$\chi_l = \frac{V_c}{3V_l - V_c}, \quad \chi_g = \frac{V_c}{3V_g - V_c}$$

The van der Waals vapour and liquid volumes are obtained for a given value of r , and by solving the pair of simultaneous equations the vapour pressure and temperature are determined.

Even though the Carnahan-Starling curve (unbroken curve in Fig. 3.4) deviates from the experimental curve for argon (dashed), the discrepancy is gratifyingly small. It is also clear from the plot that the hard core equation of state predicts gas-liquid equilibrium properties far better than the van der Waals equation (dotted curve).

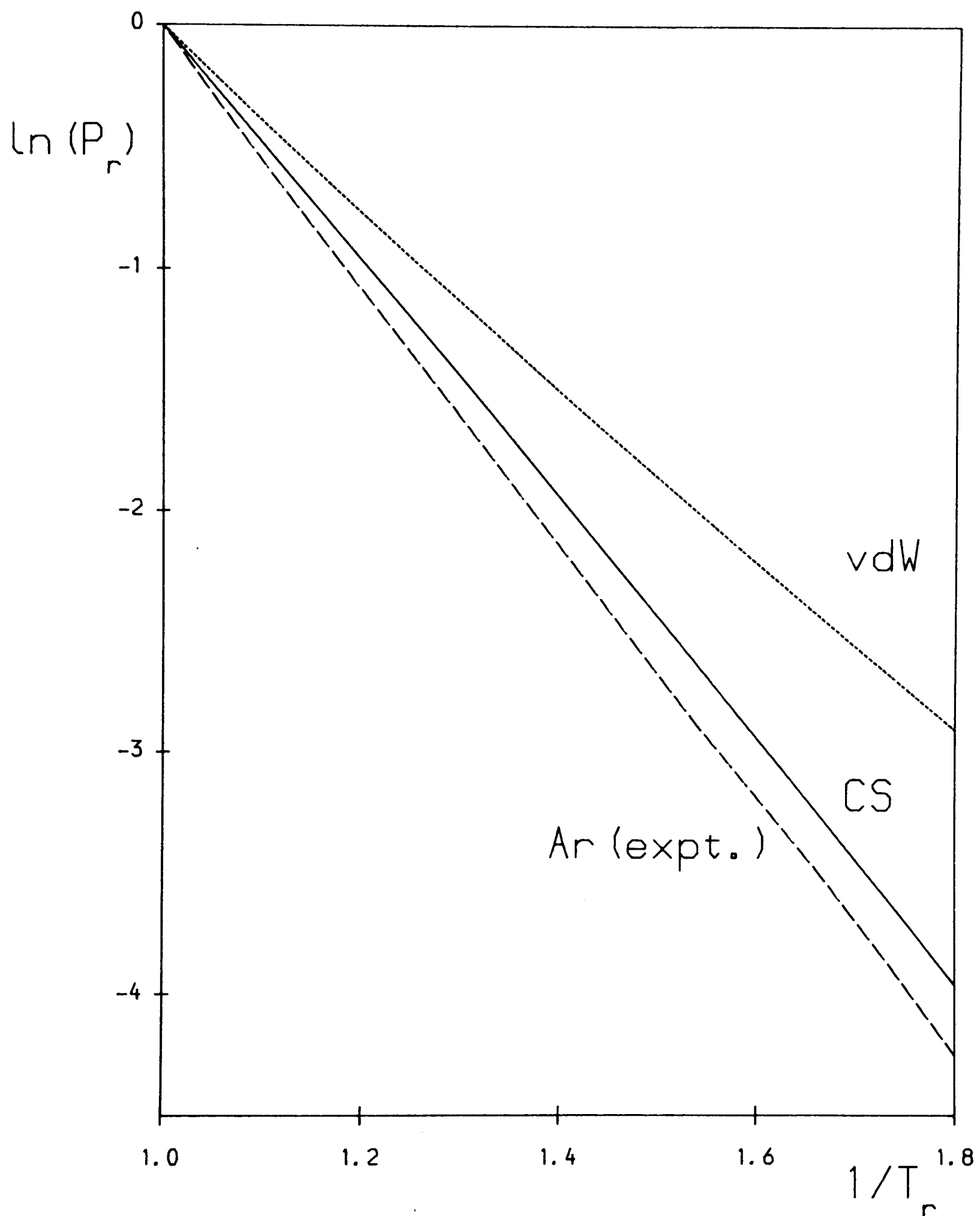


Fig. 3.4 The vapour pressure curves calculated using the Carnahan-Starling and van der Waals equations are compared with the experimental curve for argon.

The slope of the vapour pressure curve at the critical point also provides an indication of the equation's adequacy in calculating vapour pressures. For the Carnahan-Starling equation the slope can be calculated explicitly.

$$\left(\frac{\partial P_r}{\partial T_r} \right)_{v_r}^c = \frac{1 + \eta_c + \eta_c^2 - \eta_c^3}{Z_c (1 - \eta_c)^3} = \frac{Z_c^{CS}}{Z_c}$$

with,

$$\eta_c = 0.130444 \quad , \quad Z_c = 0.358956$$

$$\left(\frac{\partial P_r}{\partial T_r} \right)_{v_r}^c = 4.85246$$

This value of 4.85 compares favourably with the experimentally calculated slopes, which in the case of argon is 5.78, whilst the van der Waals value is 4.0.

All in all, the Carnahan and Starling equation with the added van der Waals attractive term provides a relatively good description of a pure fluid's gas-liquid phase equilibrium.

3.5 TEMPERATURE-DEPENDENT ATTRACTIONS

In this section, a one-component system of hard spheres with temperature-dependent attractive interactions is examined, and particular attention is paid to closed-loop coexistence. The pure hard core equation of state proposed in Section 3.1 is modified as follows:

$$P = \frac{\eta(1+\eta+\eta^2-\eta^3)RT}{b(1-\eta)^3} - F(T)\frac{a\eta^2}{b^2}$$

$$b = \frac{\pi L d^3}{6}, \quad \eta = \frac{b}{V_m}$$

As before the Carnahan-Starling equation is used to describe the system's hard sphere properties. The function $F(T)$ multiplying the van der Waals attractive term describes the temperature dependence of the attractions. Closed-loop coexistence with corresponding lower critical points is seen in this one-component hard core system when the attractive interactions between the spheres increase sharply with temperature. In this case, an appropriate function is

$$F(T) = \frac{1}{2}(1 + \tanh((RTb/a - T^*)/2\lambda^*))$$

where T^* and λ^* are adjustable parameters describing the nature of the temperature dependence. As shown in Fig. 3.5, the rate of change of $F(T)$ with temperature is greatest at T^* , whilst the magnitude of λ^* controls the sharpness of the curve's shape.

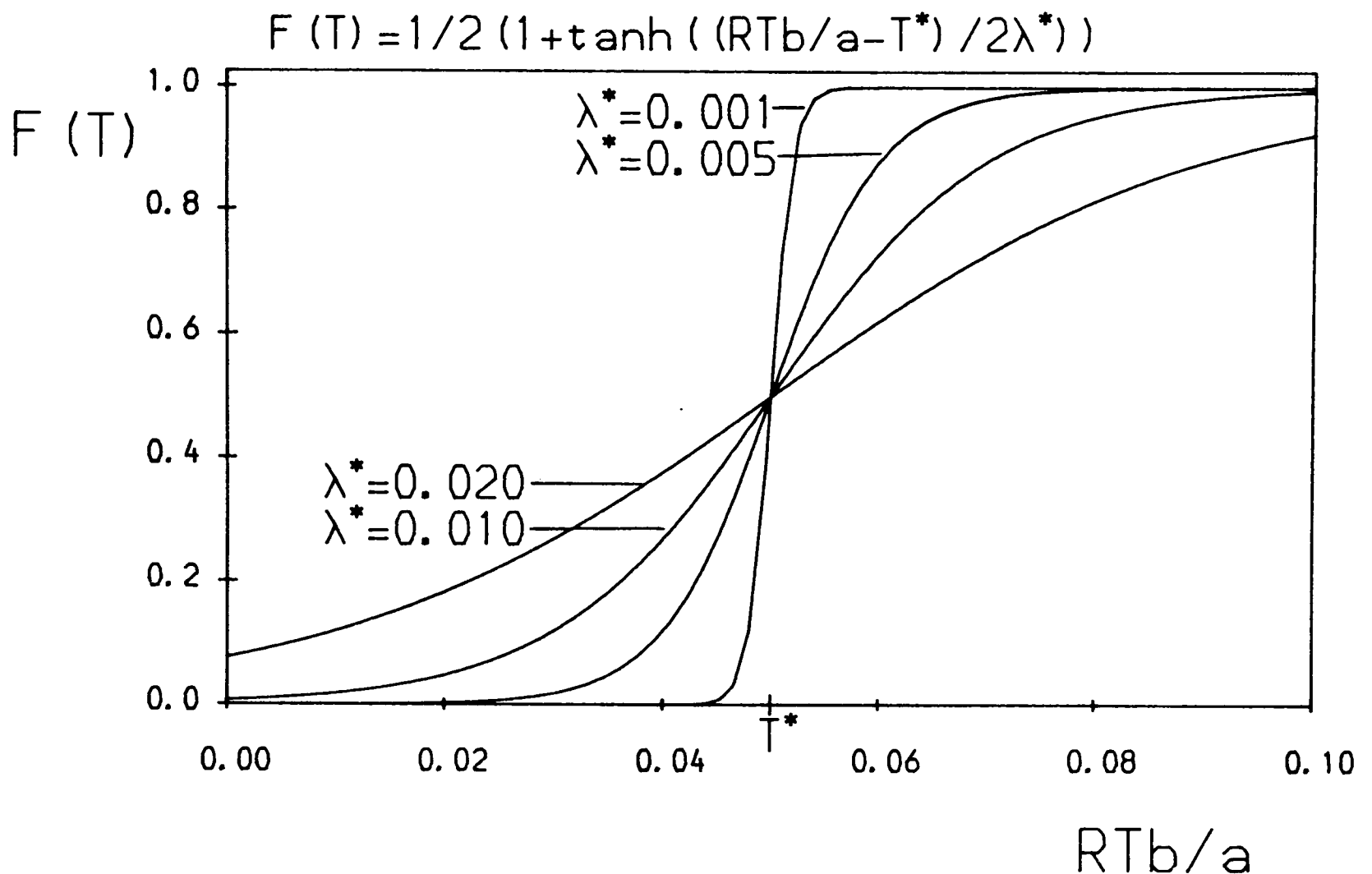
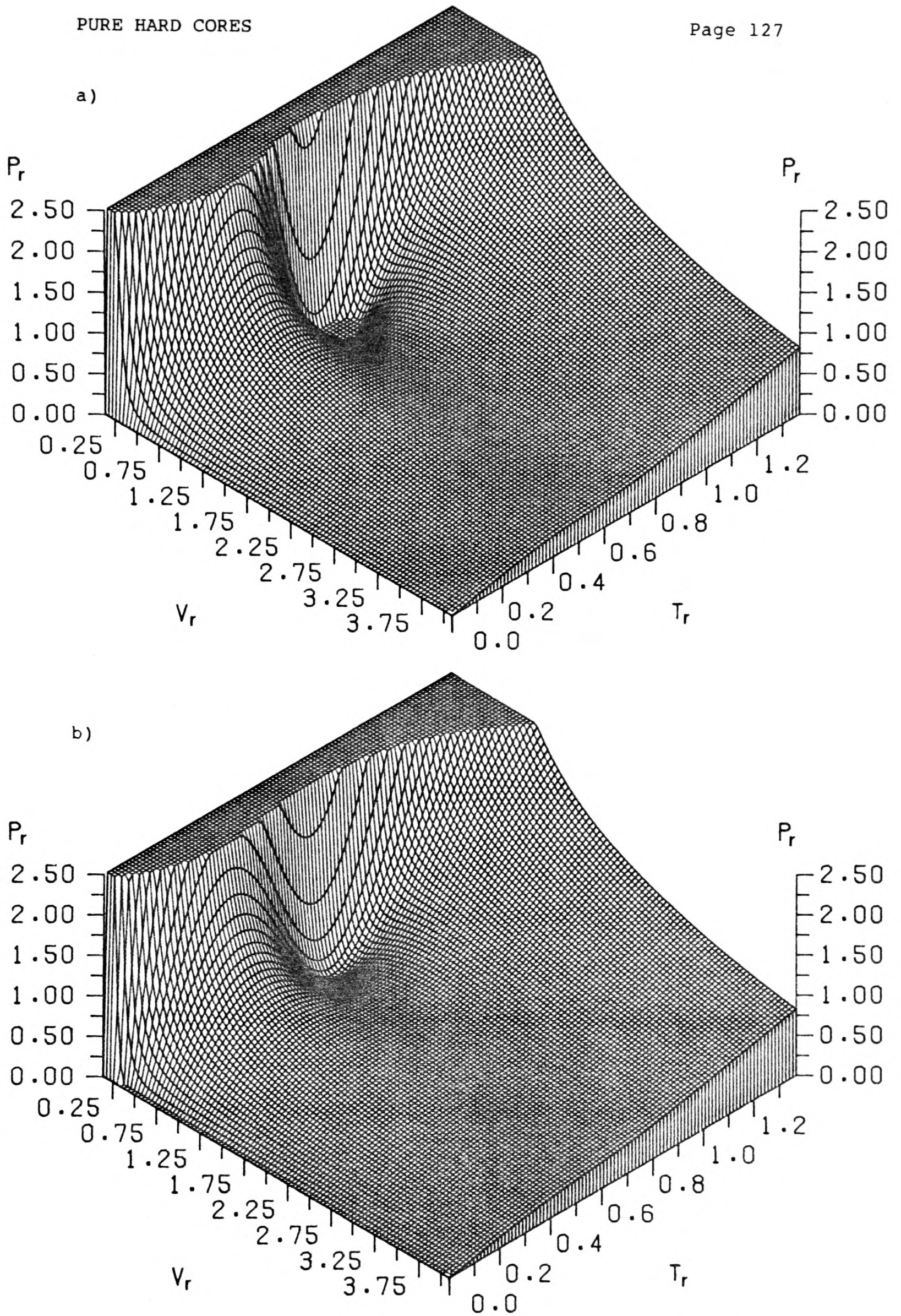


Fig. 3.5 The temperature dependence of the attractive interactions.

Fig. 3.6 represents the PVT surfaces of two systems of hard cores with temperature-dependent attractions for values of the parameters of $T^*=0.05$ and $\lambda^*=0.01$, and of $T^*=0.05$ and $\lambda^*=0.013$. The pressure, volume and temperature are reduced with respect to the critical point of the pure hard core system with constant attractive interactions described in Section 3.2. The PVT surface of the hard core system with constant attractions exhibiting the usual upper consolute coexistence was shown in Fig. 3.1. In contrast, the PVT surfaces of Fig. 3.6 for systems with temperature-dependent attractions exhibit closed-loop coexistence.



As the temperature decreases, there is a sharp increase in pressure in the region of T^* caused by the sharp fall in the attractive interactions at this point. At temperatures well below T^* , the pressure then decreases with decreasing temperature. The resulting "holes" appearing in the PVT surfaces are characteristic of the closed-loop coexistence.

The system's critical points can be obtained by solving the conditions for a gas-liquid critical point in a one-component fluid as described in Section 3.2. As with the hard cores of Section 3.2, the values of the critical density and compression factor are $\eta_c=0.130444$ and $Z_c=0.358956$. The values of the critical temperature $A_c^{-1}=bRT_c/a$ are determined by solving the following equation:

$$\frac{1}{2}(1+\tanh((bRT_c/a-T^*)/2\lambda^*)) / (bRT_c/a) - (4+10\eta_c-2\eta_c^2)/(1-\eta_c)^5 = 0$$

For certain values of T^* and λ^* three roots for the critical temperature satisfy the equation. The largest root represents the upper critical point and the middle root the lower critical point of a closed-loop coexistence curve. The third and smallest root found at very low temperatures represents the critical point of an upper consolute curve; coexistence reappears at these low temperatures because of residual attractive interactions. It must be noted that only one upper critical point is obtained when λ^* is sufficiently large.

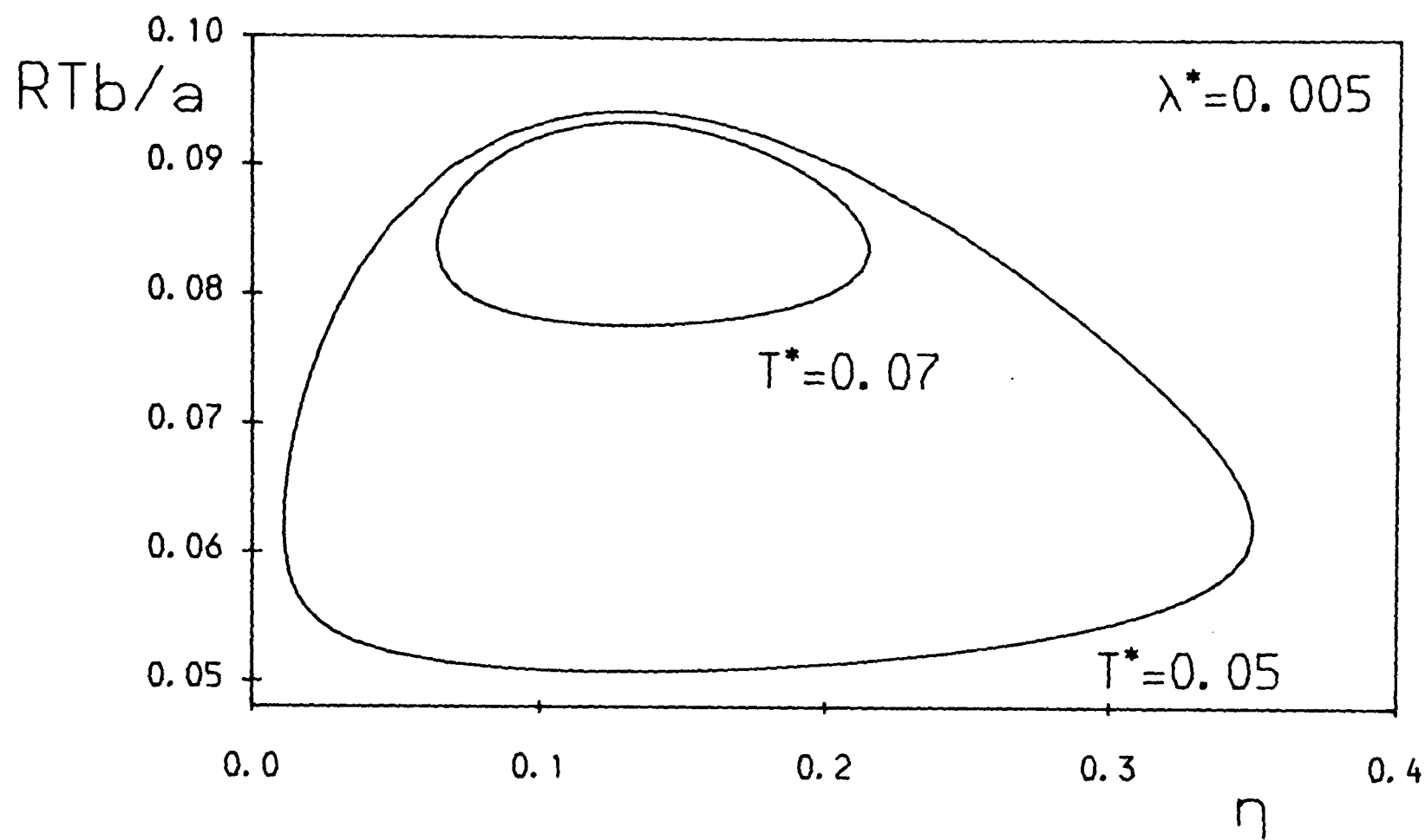


Fig. 3.7 The coexistence curves for systems with $\lambda^* \approx 0.005$ for different values of T^* .

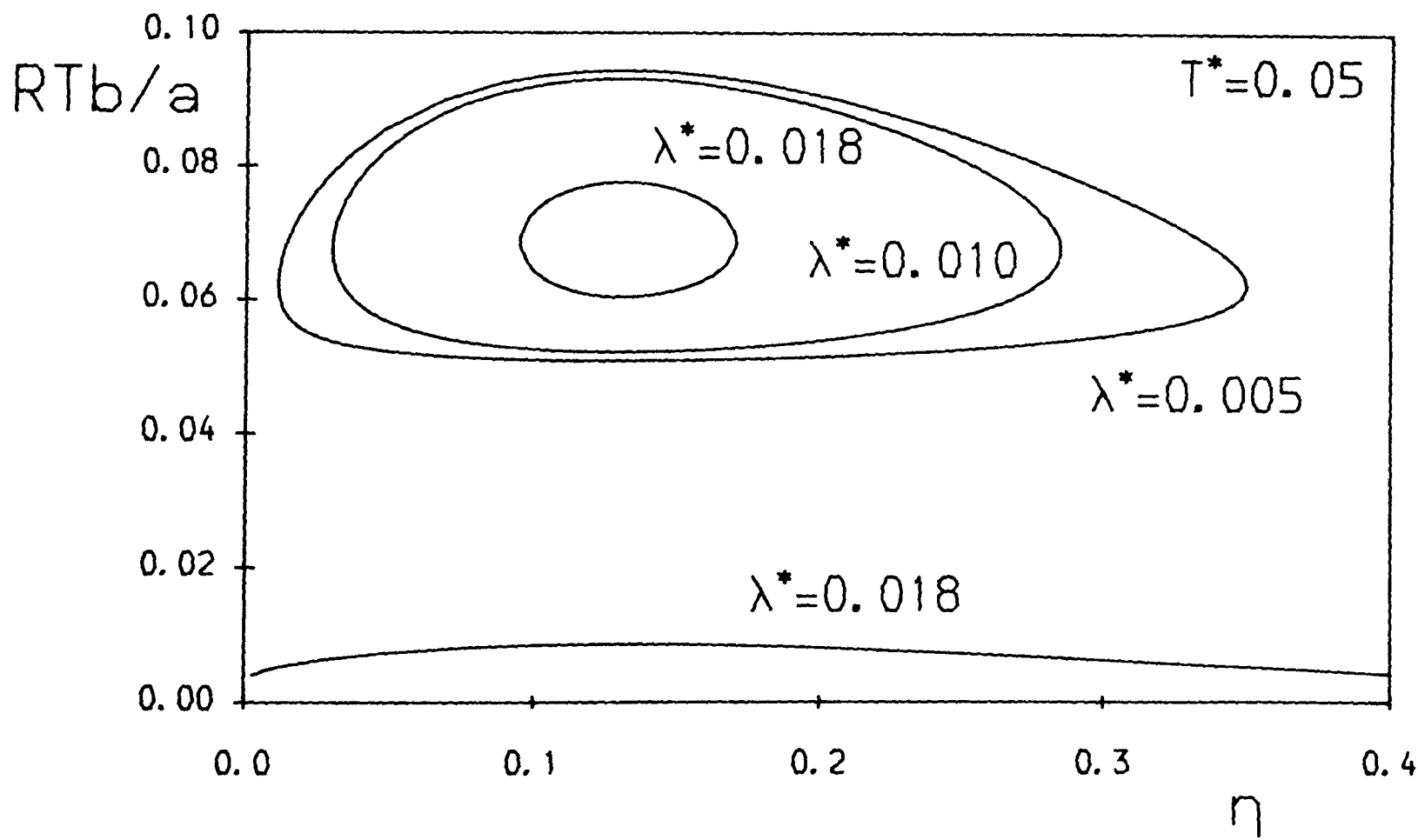


Fig. 3.8 The coexistence curves for systems with $T^* = 0.05$ for different values of λ^* .

The coexistence curves for the hard core systems with temperature-dependent attractions are determined by applying the conditions of phase equilibria. A procedure similar to the one described in Section 3.4 is used to ensure that the temperatures, pressures and chemical potentials of the coexisting phases are equal. The resulting temperature-density projections of the coexistence curves are shown in Fig. 3.7 and Fig. 3.8 for various values of T^* and λ^* . Fig. 3.7 shows the coexistence curves calculated for two values of T^* at a fixed value of $\lambda^*=0.005$. The extent of closed-loop coexistence is much greater for $T^*=0.05$ than for $T^*=0.07$. The effect that changing λ^* has on the coexistence curves of systems with a fixed value of $T^*=0.05$ is shown in Fig. 3.8. The smaller values of λ^* produce larger closed-loops with greater degrees of asymmetry. As λ^* is increased the area spanned by the closed-loop decreases until closed-loop coexistence disappears altogether; with a value of $T^*=0.05$ this occurs at about $\lambda^*>0.02$. The upper consolute coexistence curve found at low temperatures with the large value of $\lambda^*=0.018$ is due to the presence of small but non-negligible attractive interactions remaining at these temperatures.

To conclude, the results obtained in this section for the hard core systems with temperature-dependent attractive interactions are summarized. When the attractive interactions increase sharply with increasing temperature (small values of λ^*), highly asymmetric closed-loop coexistence curves are obtained which cover relatively large

areas of the phase diagram. However, for the larger values of λ^* , the attractions increase more smoothly with temperature, and consequently the extent of closed-loop coexistence diminishes and disappears altogether. Hence, the area spanned by the closed-loop coexistence curve is greatest for small T^* and λ^* .

These results can be compared with the experimental phase diagrams of aqueous micellar solutions of nonionic surfactants if the constituents of the model systems are taken to represent the single micelles. The effect of water is introduced via the effective inter-micellar potential energy which is temperature dependent. Although the exact temperature dependence of the micelle-micelle potential is not known, the comparison can yield some interesting qualitative information about the nonionic surfactant systems. In the case of polyoxyethylene($C_{10}E_5$)-water systems, the asymmetry of the experimentally determined closed-loops would suggest that the micelle-micelle attractive forces increase sharply with temperature at a temperature of about half that of the upper consolute temperature (see Chapter 8 and references therein). Presumably, there is a sharp decrease in the hydration of the micelle at this point causing an increase in the effective micelle-micelle attractive forces. The nature of closed-loop coexistence in these micellar solutions is analysed in much greater detail in Chapters 7 and 8.

CHAPTER 4

BINARY MIXTURES OF POINTS AND HARD CORES

In the first chapter of the present discussion the most accurate representation for a mixture of hard spheres was established as the equation of state proposed by Mansoori et al. which is the mixture counterpart of the Carnahan-Starling equation. The appropriate equation for a binary mixture was stated as

$$Z^{CV} = \frac{(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi) - y_3\xi^3}{(1 - \xi)^3}$$

with

$$\begin{aligned} \xi &= \sum_{i=1}^2 \eta_i = \eta_1 + \eta_2, \quad \eta_1 = \frac{\pi N_1 d_1^3}{6V}, \quad \eta_2 = \frac{\pi N_2 d_2^3}{6V} \\ y_1 &= \frac{(d_1 - d_2)^2 (d_1 + d_2) x_1 x_2}{(d_1^3 x_1 + d_2^3 x_2)}, \quad y_3 = \frac{(d_1^2 x_1 + d_2^2 x_2)^3}{(d_1^3 x_1 + d_2^3 x_2)^2} \\ y_2 &= \frac{d_1 d_2 (d_1 - d_2)^2 (d_1^2 x_1 + d_2^2 x_2) x_1 x_2}{(d_1^3 x_1 + d_2^3 x_2)^2} \end{aligned}$$

4.1 BINARY MIXTURES OF POINTS AND HARD SPHERES

The systems of interest are solutions of large spherical particles with one of the components much larger than the other. The solvent-to-solute size ratio for such a system will be very small with a limiting value of zero. In the case of a binary mixture of hard spheres this limiting value can be achieved by approximating the diameter of the smaller spheres to zero, and as a result the small spheres become point particles.

4.1.1 Mansoori Equation With $d_1=0$

Mixtures of points and hard spheres can be investigated using Mansoori's equation for hard sphere mixtures by setting one of the diameters to zero, $d_1=0$. The reduced density of the points (component 1) becomes zero, and the equation of state is expressed solely in terms of the reduced density of the spheres (component 2).

$$Z^{cv} = \frac{1 + \eta(3x_2 - 2) + \eta^2 - \eta^3 x_2}{(1 - \eta)^3}, \quad \eta = \frac{\pi N d_2^3 x_2}{6V}$$

The suffix 2 for reduced density, η , of component 2 has been dropped, and Lebowitz's functions have taken the values

$$y_1 = x_1, \quad y_2 = 0, \quad y_3 = x_2$$

By determining a point-sphere equation of state from a knowledge of the configurational integral, the equation obtained by taking the limit $d_1=0$ for the Mansoori et al. expression can be verified (see below).

4.1.2 The Configurational Integral

The configurational integral is the basis of statistical theories of fluids and for a mixture of molecules it can be calculated from a knowledge of the configurational energy, which depends on the position of the molecules and their assignment by species to these positions.

$$Q = \frac{1}{\prod_i N_i!} \int \dots \int e^{-U/kT} dr_1 \dots dr_N$$

for

$$N_1 \text{ of } 1, N_2 \text{ of } 2 \dots, \sum_i N_i = N$$

For a binary mixture of molecules 1 and 2 the configurational integral is

$$Q = \frac{1}{N_1! N_2!} \int \int e^{-U/kT} dr^{N_1} dr^{N_2}$$

and assuming pair-wise additivity of the configurational

energy the expression becomes

$$U = \frac{1}{2} \sum_i \sum_j u_{r_{ij}} = U_{11} + U_{12} + U_{22}$$

$$Q = \frac{1}{N_1! N_2!} \int_V dr^{N_2} e^{-U_{22}/kT} \int_V dr^{N_1} e^{-(U_{12}+U_{11})/kT}$$

where U_{11} and U_{22} are the configurational energies for the pure components and U_{12} is the 1-2 interaction energy.

Since we are dealing with rigid spheres the configurational energy is zero outside the sphere and infinite inside. Furthermore, when the diameter of the sphere becomes zero the configurational energy becomes everywhere zero. If there are N_2 of species 2 (hard spheres), each with a volume v , the volume excluded to species 1 (points) is $N_2 v$. Hence, the configurational integral can be integrated separately over volumes $V - N_2 v$ and $N_2 v$.

$$Q = \frac{1}{N_1! N_2!} \int_V dr^{N_2} e^{-U_{22}/kT} \left[\int_{N_2 v} dr^{N_1} e^{-(U_{12}+U_{11})/kT} + \int_{V-N_2 v} dr^{N_1} e^{-(U_{12}+U_{11})/kT} \right]$$

$= 0$

$= V - N_2 v$

$$N_2 v : U_{11} = 0, U_{12} = \infty$$

$$V - N_2 v : U_{11} = 0, U_{12} = 0$$

The configurational integral for pure hard spheres is

$$Q_2 = \frac{1}{N_2!} \int_V dr^{N_2} e^{-U_2/kT}$$

and we can now proceed to an equation of state via the configurational free energy, A' , by using the Carnahan-Starling equation for pure hard spheres.

$$Q = \frac{1}{N_1!} (V - N_2 v)^{N_1} Q_2, \quad A' = -kT \ln Q, \quad \left(\frac{\partial A'}{\partial V} \right)_T = -P$$

$$\frac{PV}{kT} = N_1 \frac{1}{(1 - N_2 v/V)} + N_2 \frac{(1 + \eta + \eta^2 - \eta^3)}{(1 - \eta)^3}$$

$$Z = \frac{1 + \eta(3x_2 - 2) + \eta^2 - \eta^3 x_2}{(1 - \eta)^3}, \quad \eta = \frac{N_2 v}{V}$$

As expected the resulting equation of state is the same as the one derived from the Mansoori equation for a binary mixture of point particles and hard spheres (see Section 4.1.1).

4.2 ATTRACTIVE INTERACTIONS IN MIXTURES

As with pure hard spheres, phase coexistence for the mixture requires the introduction of a van der Waals long-range attractive interaction, $-a/V^2$. The composition dependence of a is simply

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

and hence for a binary mixture

$$a = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2$$

where the constants a_{11} and a_{22} are measures of the attractive forces between the molecules of pure components 1 and 2, and a_{12} is the corresponding parameter for the interactions between differing species. Although these constants can take a range of values depending on the magnitudes of the actual attractions, the usual combining rules relating a_{12} to a_{11} and a_{22} that are used in theories of mixtures are the arithmetic and geometric means.

$$a_{12} = (a_{11} + a_{22})/2, \quad a_{12} = (a_{11}a_{22})^{1/2}$$

4.3 THE EQUATION OF STATE

By adding the van der Waals mean-field attractive term to the hard sphere mixture's equation of state, phase equilibria and critical behaviour are made possible. The resulting "augmented van der Waals" equation of state for hard core mixtures is

$$Z = \frac{PV}{NkT} = Z^{cv} - \frac{aN^2}{V^2} \left(\frac{V}{NkT} \right)$$

For binary mixtures of points and hard cores (see Section 4.1.1) the equation of state including the attractions is

$$P = \eta \frac{1 + \eta(3x_2 - 2) + \eta^2 - \eta^3 x_2}{bx_2(1 - \eta)^3} RT - \frac{a\eta^2}{b^2 x_2^2}$$

$$b = \pi L d_2^3 / 6, \quad \eta = x_2 b / V_m$$

$$a = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2$$

The temperature and pressure can be reduced with respect to the critical temperature and pressure of the pure hard core system described in Chapter 3 to give a reduced form of the equation. Hence, the reduced equation of state for mixtures of point particles and hard cores is given by

$$P_r = \eta \frac{1 + \eta(3x_2 - 2) + \eta^2 - \eta^3 x_2}{\eta_{c,2} Z_{c,2} x_2 (1 - \eta)^3} T_r - \frac{A_{c,2} \eta^2}{\eta_{c,2} Z_{c,2} x_2^2} (x_1^2 a_{11} / a_{22} + 2x_1 x_2 a_{12} / a_{22} + x_2^2)$$

with the pure hard core critical constants (subscript 2)

$$P_r = P / P_{c,2}, \quad T_r = T / T_{c,2}$$

$$\eta_{c,2} = 0.130444, \quad A_{c,2} = 10.6012, \quad Z_{c,2} = 0.358956$$

4.4 THE FREE ENERGY

The logarithm of the configurational integral multiplied by $-kT$ is the configurational free energy, A' . From the expression for the configurational integral determined in Section 4.1.2 we obtain

$$A' = -N_1 kT \ln V - N_1 kT \ln (1-\eta) + N_1 kT \ln N_1 - N_1 kT - kT \ln Q_2$$

and by integrating the Carnahan-Starling equation of state with respect to volume, the term involving the logarithm of the configurational integral for pure hard spheres (Q_2) is determined.

$$\left(\frac{\partial A'}{\partial V} \right)_T = -P, \quad A' = -\int P dV$$

$$A'_2 = -kT \ln Q_2 = -N_2 kT \ln V - \frac{(3\eta^2 - 4\eta)}{(1-\eta)^2} N_2 kT + C$$

The system's volume is retained in the expression for A' together with the reduced density so as to distinguish between the ideal mixture's contribution to the free energy and the deviations from ideality. C is an integration constant which can be determined by comparing our expression for the free energy with the corresponding expression for an

ideal system.

$$Q_2^{\text{ideal}} = \frac{V^{N_2}}{N_2!}$$

$$A_2'^{\text{ideal}} = -kT \ln Q_2^{\text{ideal}} = -N_2 kT \ln V + N_2 kT \ln N_2 - N_2 kT$$

$$C = kT N_2 \ln N_2 - N_2 kT$$

Therefore, the configurational free energy for a binary mixture of points and spheres is given by

$$A' = -(N_1 + N_2) kT \ln V + N_1 kT \ln N_1 + N_2 kT \ln N_2 - (N_1 + N_2) kT \\ - N_1 kT \ln(1-\eta) - \frac{(3\eta^2 - 4\eta)}{(1-\eta)^2} N_2 kT$$

The total Helmholtz free energy can be obtained from the phase integral

$$Z = \frac{1}{h^{3N_1} h^{3N_2}} \int \dots \int e^{-H/kT} dr_1 \dots dr_2 dp_1 \dots dp_2$$

$$Z = (2\pi m_1 kT/h^2)^{3N_1/2} (2\pi m_2 kT/h^2)^{3N_2/2} Q$$

and therefore the free energy, $A = -kT \ln Z$, is

$$A = N_1 \mu_1^\circ + N_2 \mu_2^\circ + N_1 kT \ln(N_1 kT/V) + N_2 kT \ln(N_2 kT/V) - (N_1 + N_2) kT \\ - N_1 kT \ln(1-\eta) - \frac{(3\eta^2 - 4\eta)}{(1-\eta)^2} N_2 kT$$

where

$$\mu_1^\circ = -kT \ln[(2\pi m_1 kT/h^2)^{3/2} kT]$$

$$\mu_2^\circ = -kT \ln[(2\pi m_2 kT/h^2)^{3/2} kT]$$

The molar Helmholtz free energy for a mixture of points and hard cores including the mean-field attractions described in Section 4.2 takes the form

$$A_m = Lx_1\mu_1^\circ + Lx_2\mu_2^\circ + x_1RT \ln(x_1RT/V_m) + x_2RT \ln(x_2RT/V_m) - RT \\ - x_1RT \ln(1-\eta) - \frac{(3\eta^2-4\eta)}{(1-\eta)^2} x_2RT - (a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2) \eta / (bx_2)$$

This equation is the starting point for the calculations of the critical lines associated with binary point-sphere mixtures; mixed derivatives of the free energy with respect to volume and composition are used to obtain the mixture's critical points (see Section 4.6).

4.5 THE CHEMICAL POTENTIALS

By differentiating the free energy with respect to the amount of each species at constant volume, we obtain the chemical potential of each component. The molar chemical potentials for the points (1) and the hard cores (2) are

$$\mu_1 = L\mu_1^\circ + RT \ln(x_1RT/V_m) - RT \ln(1-\eta) - 2(a_{11}x_1 + a_{12}x_2) \eta / (bx_2) \\ \mu_2 = L\mu_2^\circ + RT \ln(x_2RT/V_m) + \frac{x_1\eta}{x_2(1-\eta)} RT + \frac{8\eta-9\eta^2+3\eta^3}{(1-\eta)^3} RT \\ - 2(a_{12}x_1 + a_{22}x_2) \eta / (bx_2)$$

These expressions are used to determine the phase equilibria of the mixtures of point particles and hard cores (see Section 4.7).

4.6 CRITICAL POINTS IN MIXTURES

A binary mixture's critical point represents the state where two phases in equilibrium (equal temperature and pressure) become identical in density and composition. A thermodynamic consideration of the critical point yields requirements for the curvature of isothermal-isobaric sections of the $G(P,T,x)$ surface. Classically the conditions for a critical point are

$$\left(\frac{\partial^2 G_m}{\partial x^2} \right)_{T,P} = 0, \quad \left(\frac{\partial^3 G_m}{\partial x^3} \right)_{T,P} = 0$$

$$\left(\frac{\partial^4 G_m}{\partial x^4} \right)_{T,P} > 0$$

However, since the hard sphere equations express the pressure as a function of density, it is inconvenient for the calculation of the Gibbs free energy. Hence, the classical conditions for a critical point are transformed into the two equivalent equations for the Helmholtz free energy i.e.

$$A_{2V}A_{2x} - A_{Vx}^2 = 0$$

$$A_{3x} - 3A_{V2x}(A_{Vx}/A_{2V}) + 3A_{x2V}(A_{Vx}/A_{2V})^2 - A_{3V}(A_{Vx}/A_{2V})^3 = 0$$

By using the first condition, the second equation can be expressed in a more useful form

$$A_{3V}A_{2x}^2 - 3A_{2Vx}A_{Vx}A_{2x} + 3A_{V2x}A_{Vx}^2 - A_{3x}A_{2V}A_{Vx} = 0$$

The following useful notation for multiple differentiation is used

$$A_{n \times m V} = (\partial^{n+m} A / \partial^n x \partial^m V)_T$$

In the case of mixtures of hard cores, the two conditions for critical points, expressed in terms of the mixed derivatives of the Helmholtz free energy, can be solved simultaneously to eliminate the temperature. After tedious algebra a high order polynomial in reduced critical density and composition is obtained which can be solved numerically for the critical density at a given composition.

A computer program was designed to find these roots for the critical density between zero and one at a given value of the composition. It examines the sign of the polynomial for successive additions to the critical density until the sign changes, hence locating the root and enabling it to be calculated at the required accuracy by iteration. It must be noted that this procedure also calculates the equation's points of discontinuity when the function tends to plus infinity on one side of the limit and minus infinity on the other. All the roots in the range of zero to one are thus calculated.

Each root calculated at a specific composition is then used to compute the value of the reduced critical temperature which satisfies the two critical conditions. The corresponding value for the reduced critical pressure is calculated using the reduced form of the equation of state. Physically meaningless roots corresponding to negative

temperatures are not taken into account whereas roots corresponding to negative pressures are retained for further investigation.

Van Konynenburg and Scott [5] have calculated the critical lines for binary mixtures of van der Waals molecules by solving the appropriate conditions in a similar way.

4.7 PHASE EQUILIBRIA

Since the hard core equations are continuous through the gas and liquid states via metastable and unstable regions, all gas-liquid and liquid-liquid critical points, whether stable, metastable or unstable, are calculated when the critical lines are determined. An investigation of the system's pressure-temperature-composition, PTx, phase surface will determine which critical lines or portions of a line are thermodynamically stable and which are not.

For two phases to coexist in a binary system, the temperature and pressure of each phase must be the same and the chemical potential of each component in one phase must equal its chemical potential in the other phase. These conditions are sufficient to calculate the details of the PTx surface.

$$P^{\alpha} = P^{\beta} , \quad T^{\alpha} = T^{\beta} , \quad \mu_1^{\alpha} = \mu_1^{\beta} , \quad \mu_2^{\alpha} = \mu_2^{\beta}$$

The logarithm of the activities for each component and the Gibbs free energy are defined by the equations

$$\ln \lambda_1 = (\mu_1 - \mu_1^\circ) / RT, \quad \ln \lambda_2 = (\mu_2 - \mu_2^\circ) / RT$$

$$(G - G^\circ) / RT = x_1 \ln \lambda_1 + x_2 \ln \lambda_2$$

and these expressions can be used to determine the mixture's phase equilibria.

If the mixture's equation of state is solved numerically for the reduced density at a constant pressure and temperature and at a given value of the composition, three roots are obtained: the root with the lowest density represents the gas phase whilst the high density root represents the liquid phase (the middle root is discarded). The reduced temperature, pressure and composition together with the corresponding value of the density are then used to calculate the logarithm of the activities and the Gibbs free energy for both the gas and liquid roots. This procedure is repeated for different values of the composition so that a series of gas activities and a series of liquid activities are obtained spanning the entire composition range for fixed values of the temperature and pressure. In turn a series of gas and of liquid Gibbs free energies are also obtained which can then be plotted against composition as shown in Fig. 4.1. It must be noted that this plot and others presented in this section correspond to the binary mixture of points and hard cores with $a_{11}=0$ and $a_{12}=a_{22}/2$ described in Section 4.8.2. The unstable curves representing the middle root are omitted.

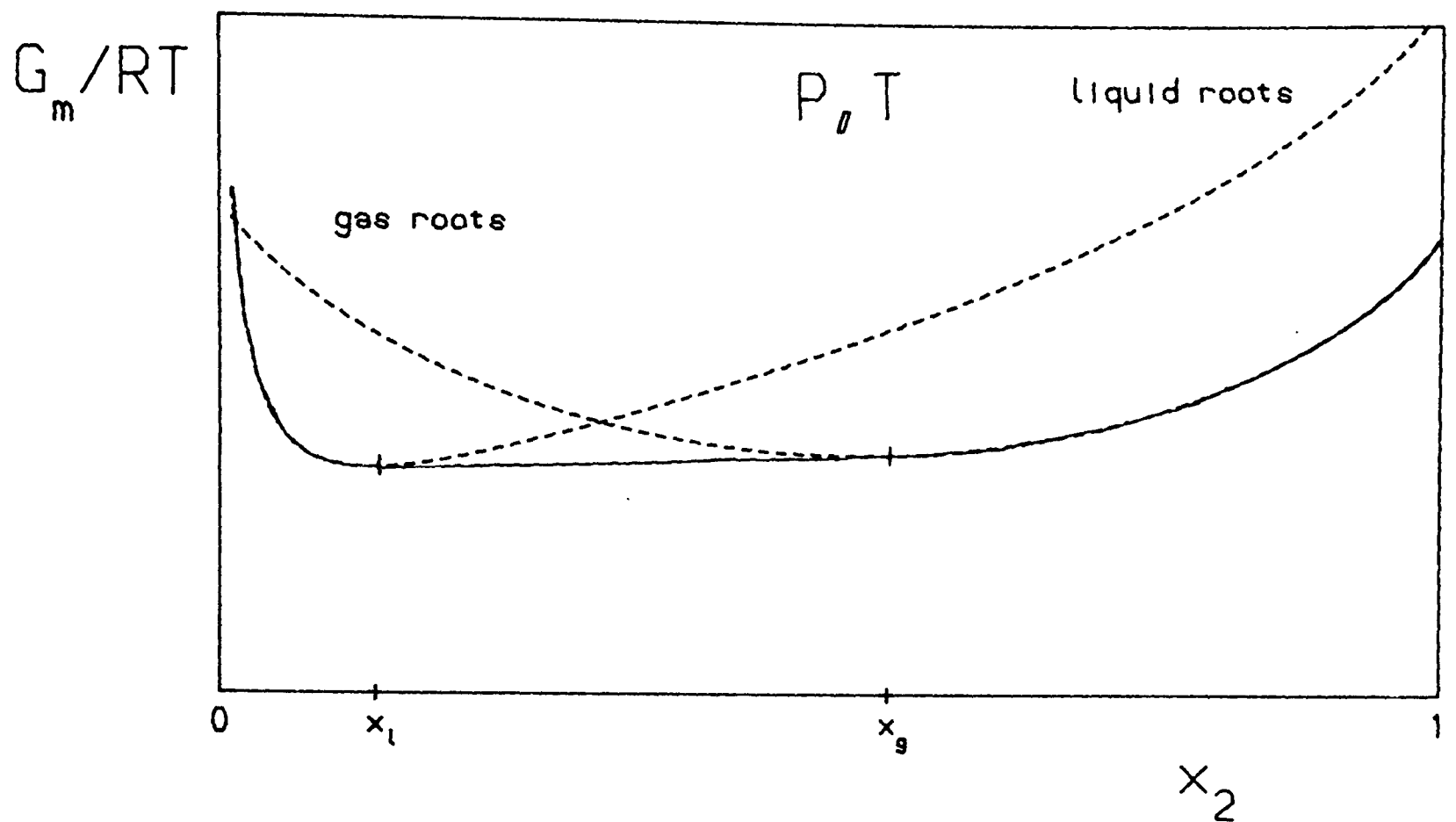


Fig. 4.1 Isothermal-isobaric plots of the Gibbs free energy against mole fraction showing gas-liquid coexistence.

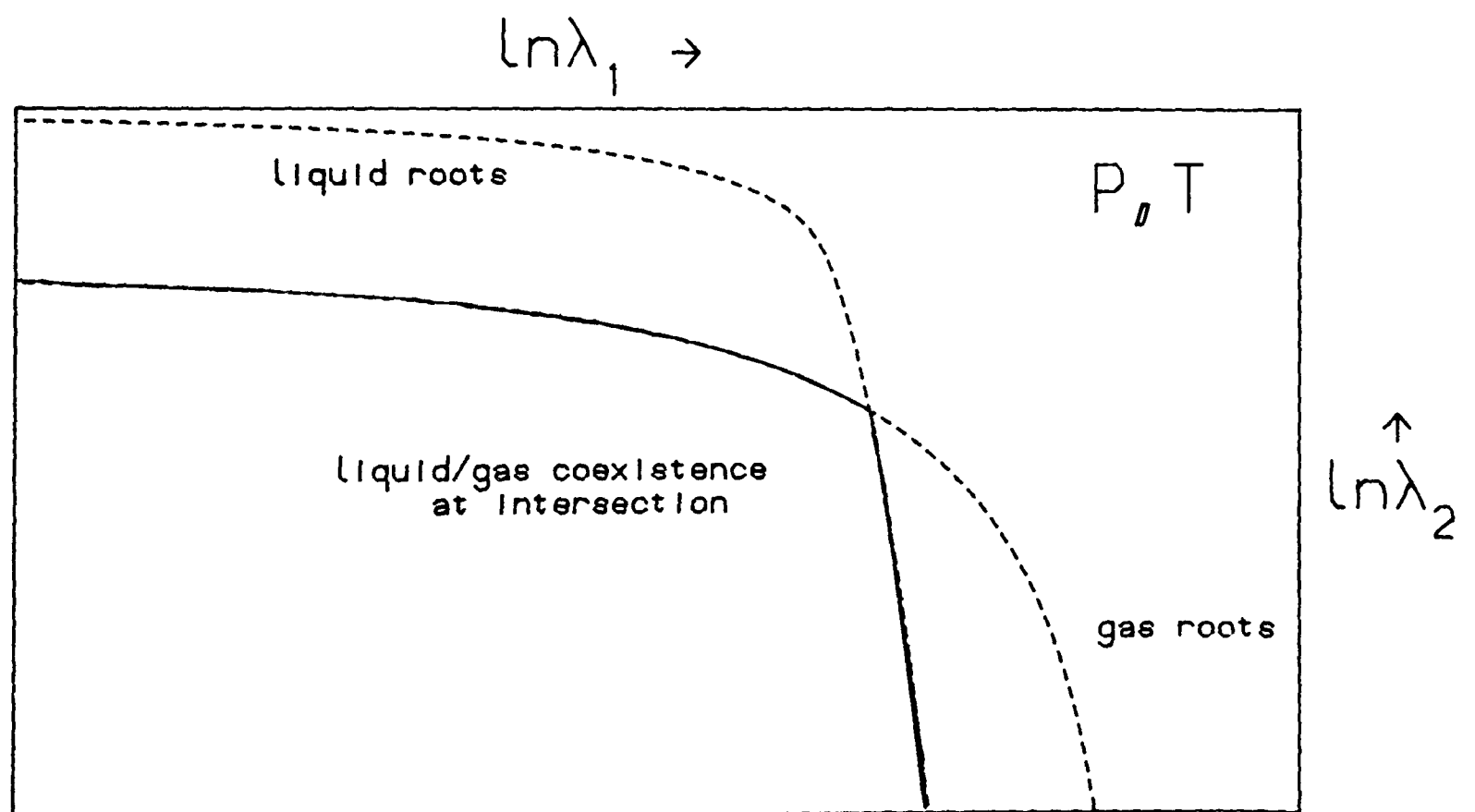


Fig. 4.2 Activity plots representing gas-liquid coexistence at a given temperature and pressure.

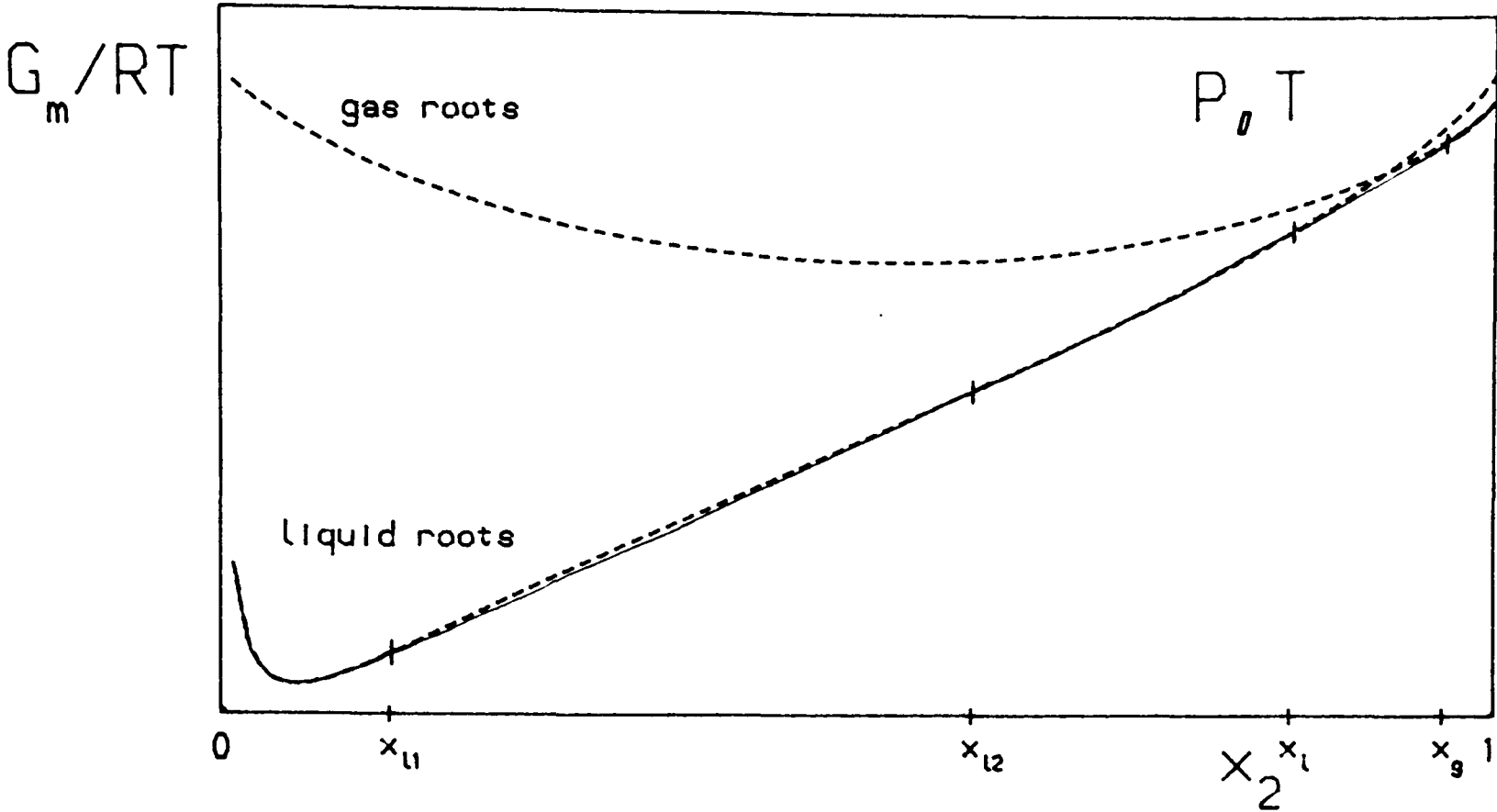


Fig. 4.3 Gibbs free energy plots for a system with both gas-liquid and liquid-liquid coexistence.

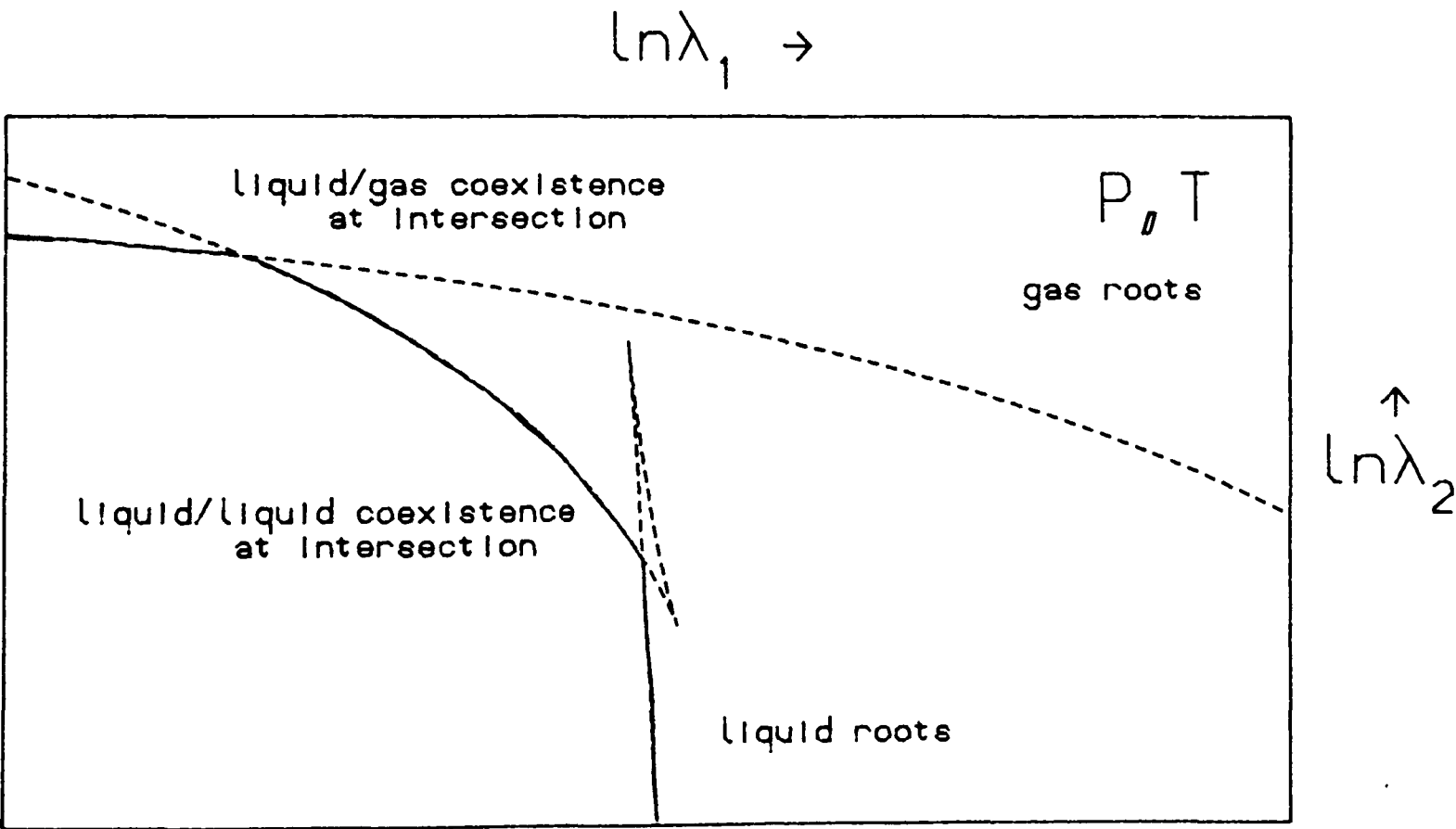


Fig. 4.4 Activity plots representing gas-liquid and liquid-liquid coexistence.

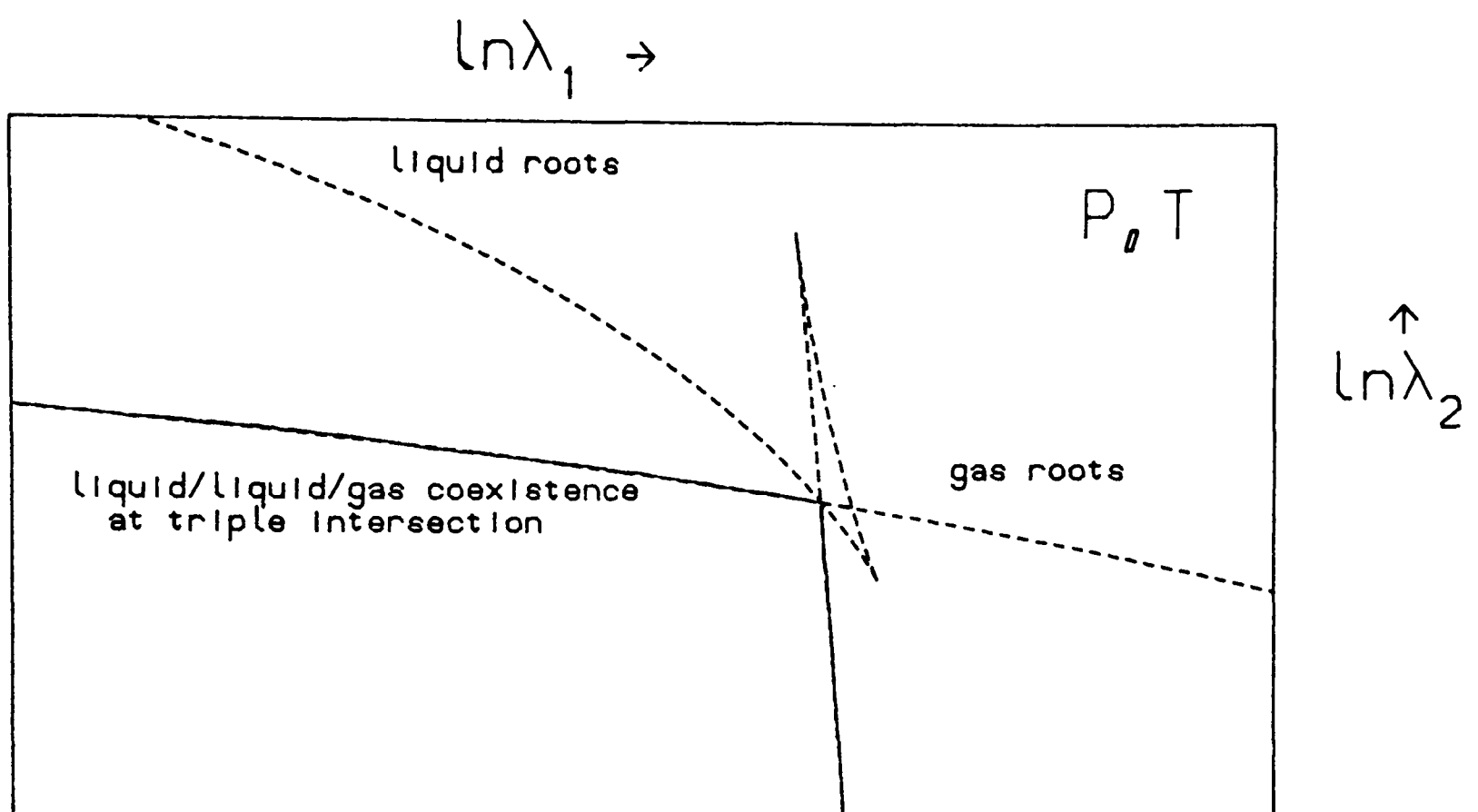


Fig. 4.5 Activity plots at a temperature and pressure corresponding to liquid-liquid-gas three phase coexistence.

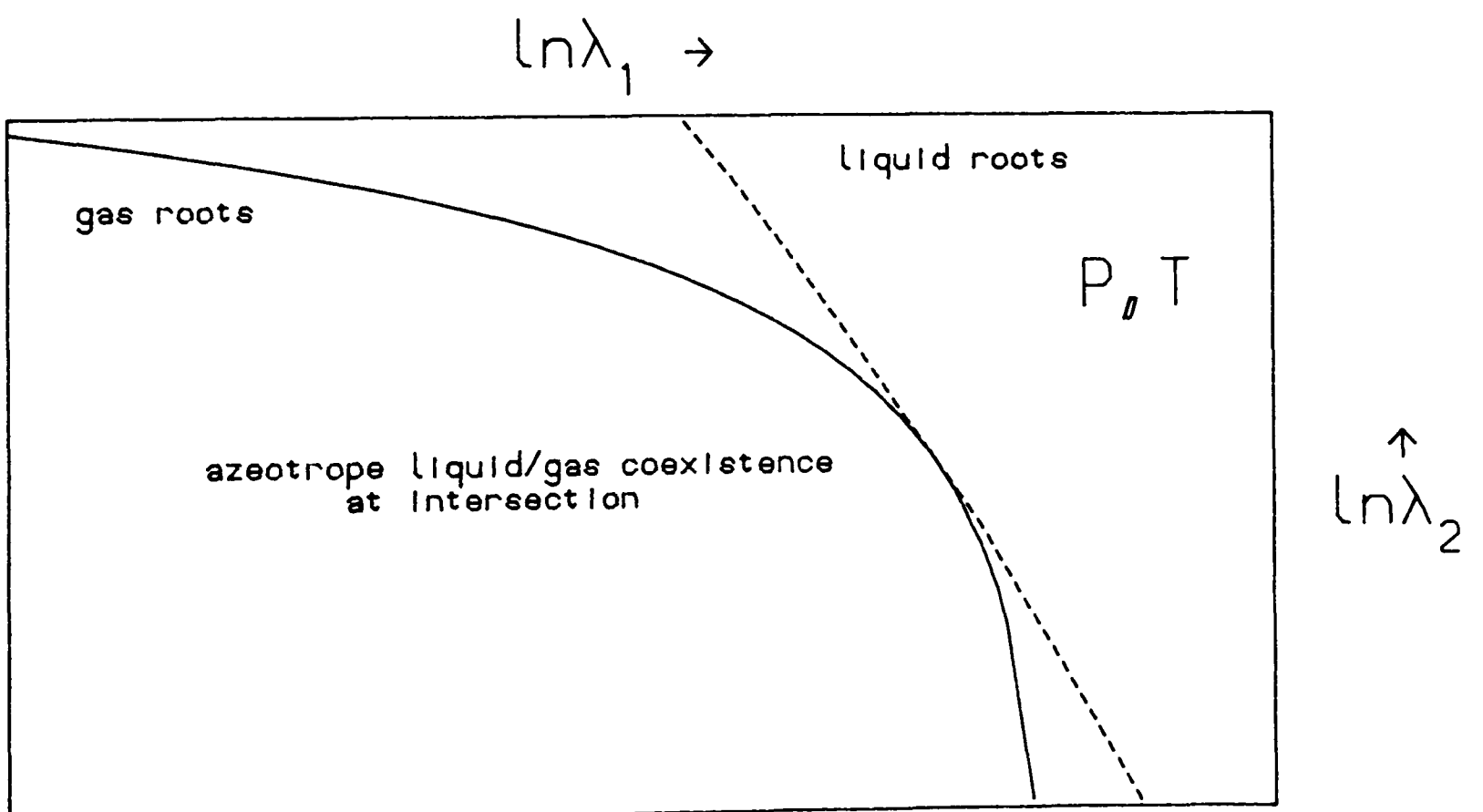


Fig. 4.6 Activity plots for gas-liquid coexistence at an azeotropic point.

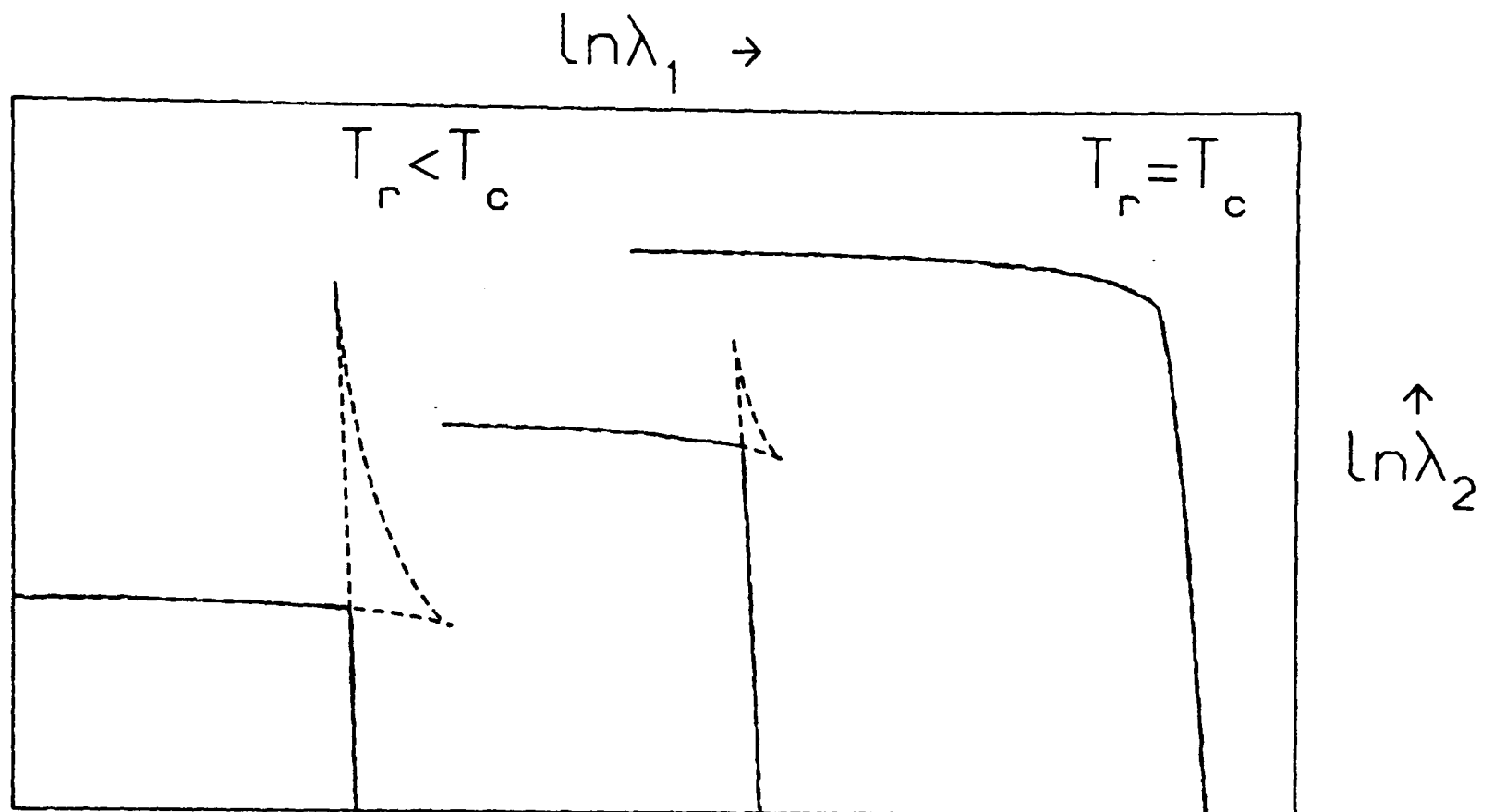


Fig. 4.7 Activity plots for three isotherms near a liquid-liquid upper critical solution temperature (UCST).

For values of the free energy along the metastable and unstable (dashed) portions of the curves in Fig. 4.1, the system can lower its free energy by separating into two phases with compositions x_l and x_g determined by the points where a straight line meets the curve at a tangent. This particular example is for gas-liquid coexistence corresponding to a reduced temperature of $T_r=0.8749$ and a reduced pressure of $P_r=0.2000$ in the pressure-composition phase diagram of Fig. 4.14(c). The corresponding constant pressure and temperature activity plots are given in Fig. 4.2. Two phases coexist when the chemical potential of

each component in one phase is equal to its chemical potential in the other phase. Hence, like the tangent in Fig. 4.1 the point of intersection on the activity plots defines the compositions of the coexisting phases with the equality of chemical potentials.

In certain regions of the phase diagram both gas-liquid and liquid-liquid coexistence are observed. The corresponding Gibbs free energy plots are depicted in Fig. 4.3 with the two pairs of coexisting compositions, and the activity plots are shown in Fig. 4.4. These figures represent a reduced temperature of $T_r=0.7199$ and a pressure of $P_r=0.1350$ on the pressure-composition phase diagram shown in Fig. 4.14(a).

Other special features of phase equilibria such as three phase coexistence, azeotropy and upper critical solution temperatures are examined next. Three phase coexistence requires that the chemical potential of each component is the same in each of the three phases so that on the activity plots the three lines must intersect at one point. An example of liquid-liquid-gas coexistence is shown in Fig. 4.5 corresponding to a reduced temperature of $T_r=0.7199$ and a pressure of $P_r=0.1168$ on Fig. 4.14(a).

Some of the systems investigated also show azeotropy with the compositions and chemical potentials of each component in each phase being equal. Fig. 4.6 shows the activity plots obtained at the azeotropic point representing a temperature of $T_r=0.7199$ and a pressure of $P_r=0.0141$ on Fig. 4.14(a).

Finally, the disappearance of liquid-liquid coexistence as the temperature is increased towards the upper critical solution temperature (UCST) is depicted in terms of activity plots in Fig. 4.7.

By taking advantage of the geometry governing the activity plots, a computer program is used to calculate the points of intersection so that the reduced densities and compositions of the coexisting phases are established at a given temperature and pressure. If this procedure is repeated at the same reduced temperature but at different pressures, the complete isothermal pressure-composition, P_x , phase diagram is obtained. Conversely, keeping the pressure fixed and varying the temperature determines the isobaric temperature-composition, T_x , phase diagram.

A similar program is also used to calculate the temperature, pressure, densities and compositions for three phase coexistence, occurring at the point of triple intersection on the activity plots. The liquid-liquid-gas lines and temperature-density phase diagrams are then obtained by varying the temperature until an upper critical end point (UCEP) or a lower critical end point (LCEP) is reached.

4.8 CRITICAL LINES AND PHASE DIAGRAMS

4.8.1 System With $a_{11}=0$, $a_{12}=0$ And $a_{22}>0$

The simplest possible mixture of point particles and hard core molecules showing phase separation is a system with no attractive interactions between the points, attractive interactions between the spheres, and no point-sphere attractions. In effect a_{12} is the geometric mean of the point-point (11) and sphere-sphere (22) attractive interactions.

$$a_{11} = 0 \quad , \quad a_{12} = 0 \quad , \quad a_{22} > 0$$

An equation of state for such a system is obtained from the expression for binary mixtures of points and spheres with an appropriate van der Waals attractive term (Section 4.3). If the temperature and pressure are reduced with respect to the critical temperature and pressure of the pure hard core system, the reduced form of the equation is

$$P_r = \frac{\eta (1 + \eta (3x_2 - 2) + \eta^2 - \eta^3 x_2) T_r}{\eta_{c,2} Z_{c,2} x_2 (1 - \eta)^3} - \frac{A_{c,2} \eta^2}{\eta_{c,2} Z_{c,2}}$$

with

$$P_r = P/P_{c,2} \quad , \quad T_r = T/T_{c,2}$$

$$\eta_{c,2} = 0.130444 \quad , \quad A_{c,2} = 10.6012 \quad , \quad Z_{c,2} = 0.358956$$

4.8.1.1 The Critical Line -

The mixture's critical line is determined by solving the conditions for critical points in binary mixtures as described in Section 4.6. From the appropriate derivatives of the Helmholtz free energy, the first condition for a critical point is

$$D = A_{2V}A_{2x} - A_{Vx}^2 = 0$$

$$D = \frac{R^2 T_c^2}{x^3 (1-x) b^2} \left[\eta_c^2 \frac{(-1 - 4\eta_c - 4\eta_c^2 + 4\eta_c^3 - \eta_c^4)}{(1-\eta_c)^4} + 2A_c \eta_c^3 \right] = 0$$

$$b = \pi L d_2^3 / 6, \quad \eta_c = bx / V_c, \quad A_c = a / (bRT_c)$$

where η_c is the critical density, x the critical composition ($x=x_2$), and A_c is an appropriate function of temperature.

The second condition can be written

$$D_x dx + D_V dV = 0 \quad \text{or} \quad D_\eta = 0$$

$$D_\eta = \frac{R^2 T_c^2}{x^3 (1-x) b^2} \left[-\eta_c \frac{(2 + 14\eta_c + 20\eta_c^2 - 20\eta_c^3 + 10\eta_c^4 - 2\eta_c^5)}{(1-\eta_c)^5} + 6A_c \eta_c^2 \right] = 0$$

and solving simultaneously we obtain the roots

$$\eta_c^5 - 5\eta_c^4 + 4\eta_c^3 + 20\eta_c^2 + 5\eta_c - 1 = 0$$

$$\eta_c = 0.130444, \quad A_c = 10.6012$$

These are identical to the roots calculated for pure hard cores using the Carnahan-Starling equation. It is clear that the roots obtained are independent of composition so that there is no change in the reduced critical density and temperature upon mixing (there is a discontinuity at zero composition). If we calculate the reduced critical pressure at these points from the equation of state, it is found that the pressure increases as the composition of spheres decreases (Fig. 4.9(d)).

The corresponding pressure-temperature projection of the pressure-temperature-composition, PTx, surface for the binary mixture of hard cores and non-interacting points is shown in Fig. 4.8.

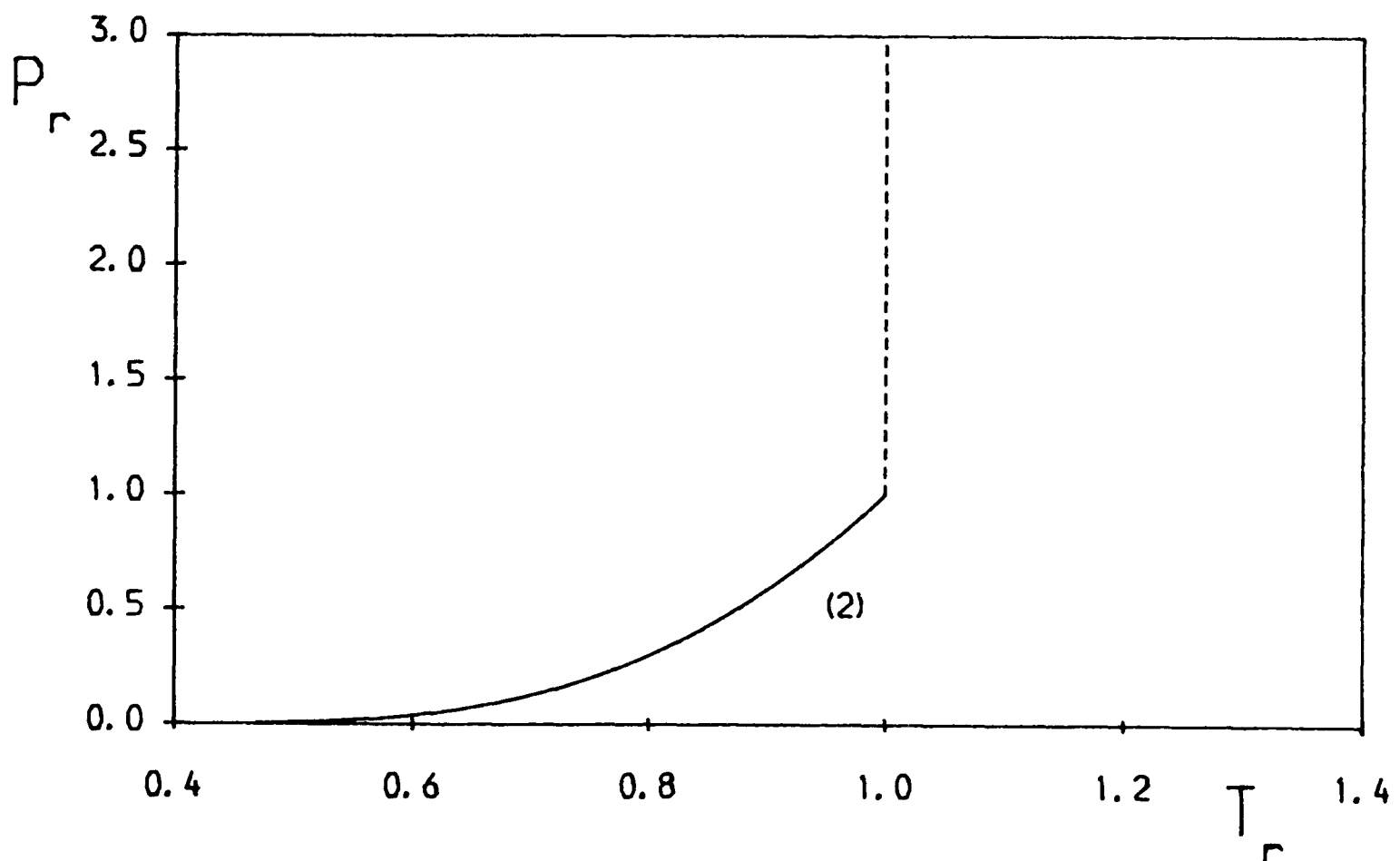


Fig. 4.8 The pressure-temperature projection for a mixture of points and hard cores with $a_{11}=0$ and $a_{12}=0$.

4.8.1.2 Transcription To A One-Component System -

The point-hard core mixture with $a_{11}=0$ and $a_{12}=0$ is a special case in that its phase equilibrium properties can be derived easily from those of the pure hard core system described in Chapter 3. In the McMillan-Mayer solution theory [51], the solute is treated as a quasi-one-component system, with the solvent playing an implicit background role through its influence on the partition function. Rowlinson [52] has described the general method of transcribing the grand partition function of an m -component system to a system of $m-1$ components when the component that is being averaged out has no intermolecular interactions with molecules of its own species. The point-hard core mixture of interest complies with these requirements since $a_{11}=0$, and the mixture can be transcribed to a one-component hard core system, with the points providing an essentially background influence.

The equations quoted in the following section are described in Rowlinson's paper. The pair potential for a mixture of two components is given by

$$\begin{aligned} U(r_1^m, r_2^n) &= U_{11}(r_1^m) + U_{12}(r_1^m, r_2^n) + U_{22}(r_2^n) \\ &= U_{12}(r_1^m, r_2^n) + U_{22}(r_2^n) \end{aligned}$$

In the case of the mixture of points and spheres, the point-point pair potential U_{11} is zero since $a_{11}=0$, the point-sphere pair potential U_{12} simply involves the excluded volume $V-nw_1$ since $a_{12}=0$, and the sphere-sphere pair potential is given by U_{22} . The cluster volume defined by

Rowlinson's equation (5.2) is

$$\begin{aligned} W(r_2^n) &= \int_V dr_1 [1 - \exp(-U(r_1, r_2^n)/kT)] \\ &= V - \exp(-U_{22}(r_2^n)/kT) \int_V dr_1 \exp(-U_{12}(r_1, r_2^n)/kT) \\ &= V - (V - nw_1) \exp(-U_{22}(r_2^n)/kT) \end{aligned}$$

and from equation (5.4) we have

$$\begin{aligned} \int_V dr_1^{N_1} \exp(-U(r_1^{N_1}, r_2^n)/kT) &= (V - W(r_2^n))^{N_1} \exp[(N_1 - 1)U_{22}(r_2^n)/kT] \\ &= (V - nw_1)^{N_1} \exp(-U_{22}(r_2^n)/kT) \end{aligned}$$

When γ_2 is defined by (5.3) and $\bar{E}_1$ by (5.5), the effective potential between molecules of the set 2 is obtained from (1.1) and (2.1):

$$\gamma_2 = \exp(-\lambda_1 w_1 / \Lambda_1^3) \lim_{\lambda_2 \rightarrow 0} (\lambda_2 / \rho_2 \Lambda_2^3), \quad \bar{E}_1 = \exp(\lambda_1 V / \Lambda_1^3)$$

$$\begin{aligned} \exp(-\bar{U}_{22}(r_2^n)/kT) &= \gamma_2^{-n} g^{(n)}(r_2^n, \lambda_2 \rightarrow 0) \\ &= \exp(\lambda_1 n w_1 / \Lambda_1^3) \bar{E}_1^{-1} \sum_{N_1} \frac{(\lambda_1 / \Lambda_1^3)^{N_1}}{N_1!} \int_V dr_1^{N_1} \exp(-U(r_1^{N_1}, r_2^n)/kT) \\ &= \exp(-\lambda_1 (V - n w_1) / \Lambda_1^3) \sum_{N_1} \frac{(\lambda_1 / \Lambda_1^3)^{N_1}}{N_1!} (V - n w_1)^{N_1} \exp(-U_{22}(r_2^n)/kT) \\ &= \exp(-\lambda_1 (V - n w_1) / \Lambda_1^3) \exp(-U_{22}(r_2^n)/kT) \exp(\lambda_1 (V - n w_1) / \Lambda_1^3) \end{aligned}$$

$$\therefore \bar{U}_{22}(r_2^n) = U_{22}(r_2^n)$$

Therefore the effective intermolecular potential for the transcribed point-hard core mixture is the same as the pure hard core system's potential. In thermodynamic terms this means that the mixture's hard core chemical potential will be the same as the pure system's chemical potential for the same N, V, T . The equivalence of the transcribed and the pure systems implies that the mixture's critical temperature, critical density and gas-liquid coexistence densities at a given temperature are the same as those calculated for the pure hard cores. These results are quite general for binary mixtures involving point particles with $a_{11}=0$ and $a_{12}=0$ and are not just restricted to hard core pair potentials; Rigby et al. [53] have reported similar results for mixtures of point particles and square well molecules.

4.8.1.3 Pressure-Composition Phase Diagrams -

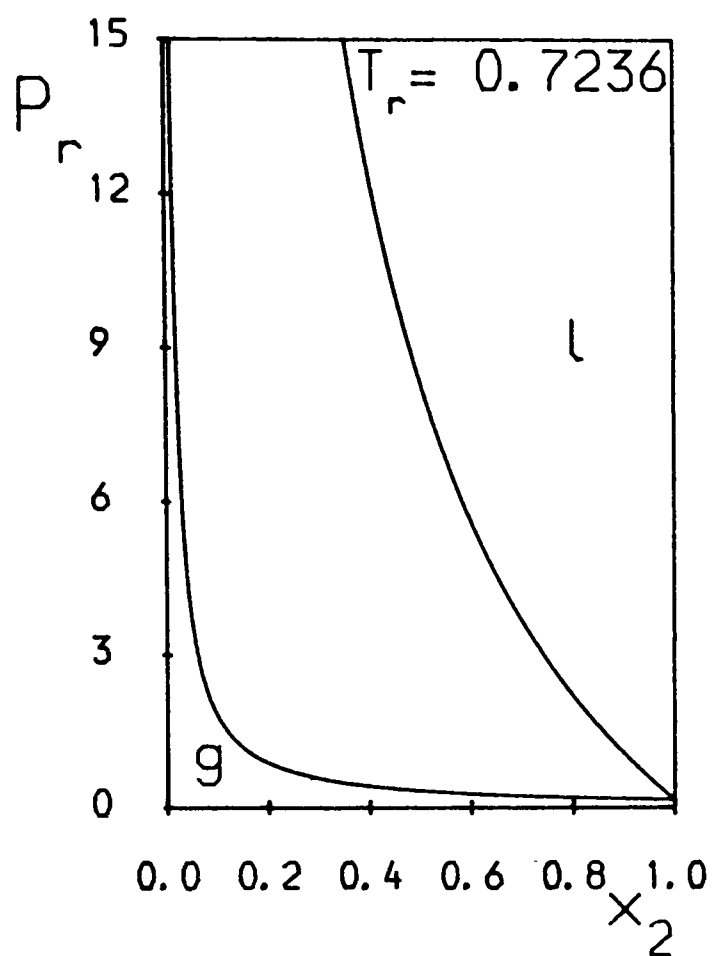
The pressure-composition, P_x , constant-temperature slices of the PT_x surface are calculated by using the results for the pure hard cores. At a given temperature along the vapour pressure curve of the pure hard cores, the liquid and gas coexistence densities are calculated (see Section 3.4). Using these values for the temperature and coexisting densities, the equation of state for the point-hard core mixture (Section 4.8.1) is then solved numerically at a given value of the pressure, yielding the coexistence compositions of the gas and liquid phases. This procedure is then repeated for other values of the pressure so that the complete P_x phase diagram is obtained.

The calculated isothermal pressure-composition slices are shown in Fig. 4.9(a-d). As the composition of the hard cores approaches the limiting value of zero, the pressure tends to infinity due to the fact that the system of pure points does not have well-defined vapour pressures. Furthermore, when the temperature is increased, the extent of gas-liquid coexistence decreases until at a reduced temperature of unity, all the critical points at different compositions appear simultaneously (see Fig. 4.9(d)).

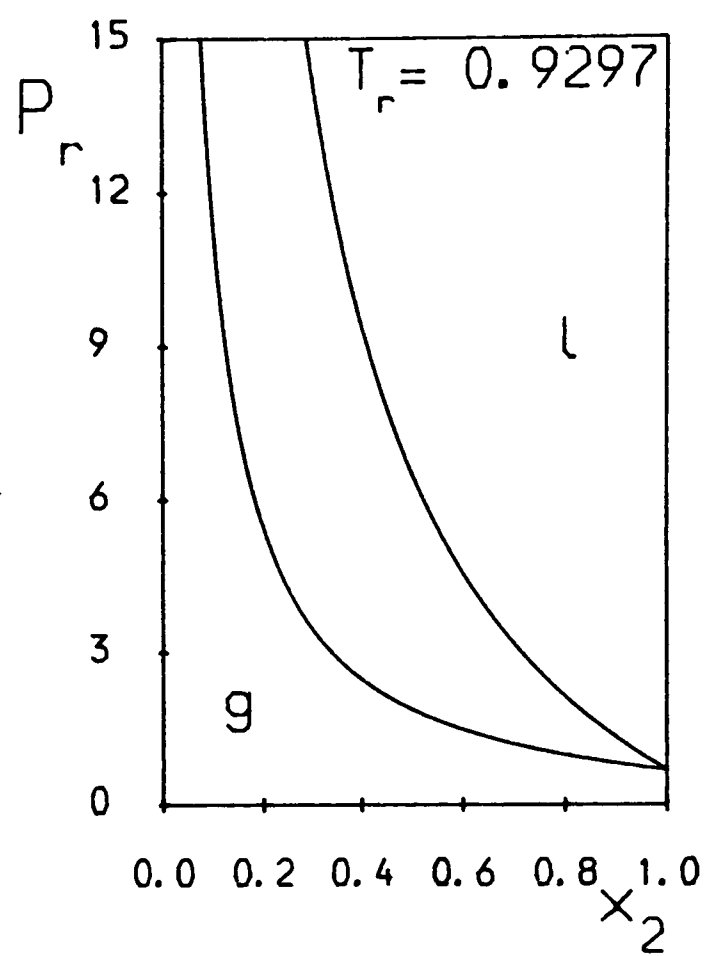
By calculating a series of P_x slices at different temperatures, the pressure-temperature-composition, PT_x , surface is determined. A three-dimensional plot of this surface is shown in Fig. 4.10 at two different orientations, and both the dew-point surface (gas compositions) and the bubble-point surface (liquid compositions) are seen.

We now progress from binary mixtures of points and hard cores without point-sphere attractive interactions to point-hard core mixtures which have point-sphere attractions. The presence of these attractions enhances the richness of phase behaviour seen in the phase diagrams with the appearance, amongst other features, of liquid-liquid coexistence.

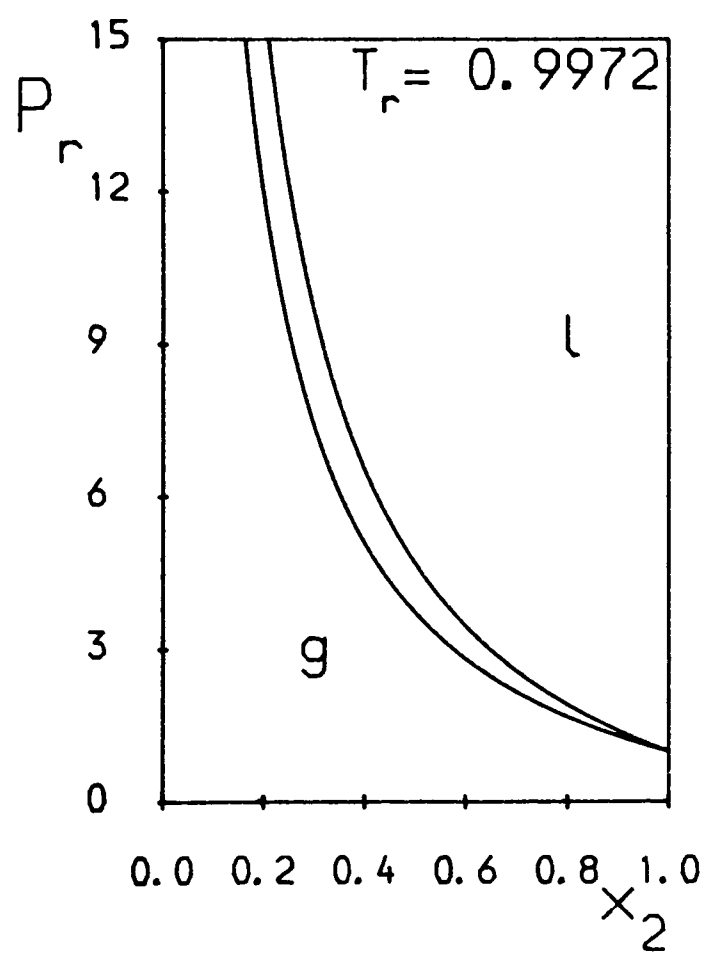
It must be noted that when the point-hard core attractions are not zero, the transcription of the mixture's properties to those of a quasi-one-component system becomes quite difficult. Instead the thermodynamic techniques described in Sections 4.6 and 4.7 are employed to determine the mixture's critical lines and phase equilibria.



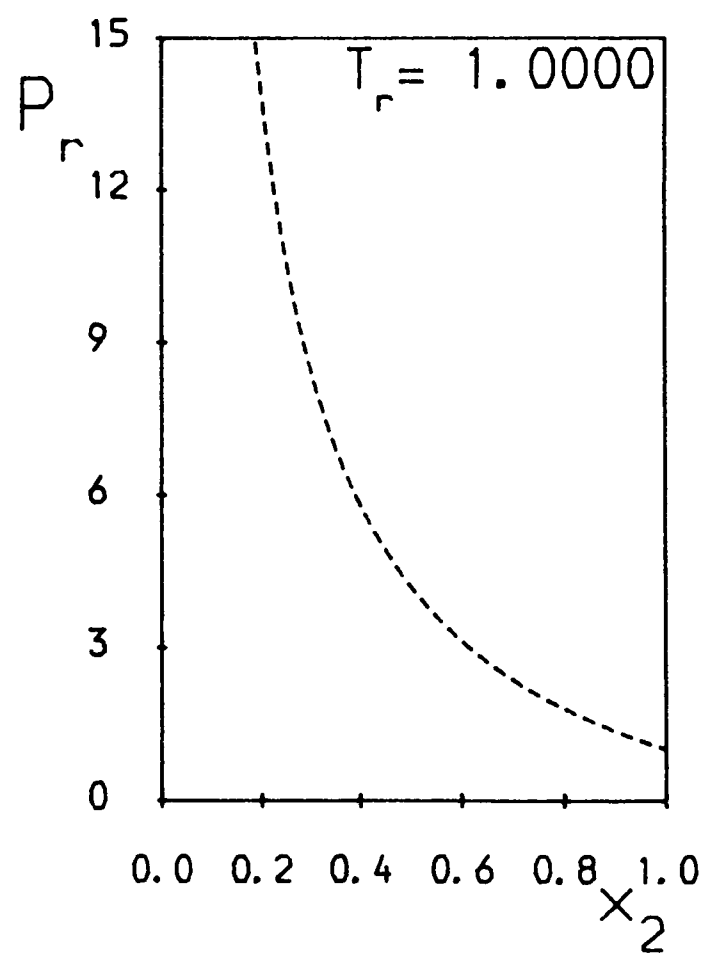
(a)



(b)



(c)



(d)

Fig. 4.9 Isothermal pressure-composition phase diagrams for a mixture of points and hard cores with $a_{11}=0$ and $a_{12}=0$.

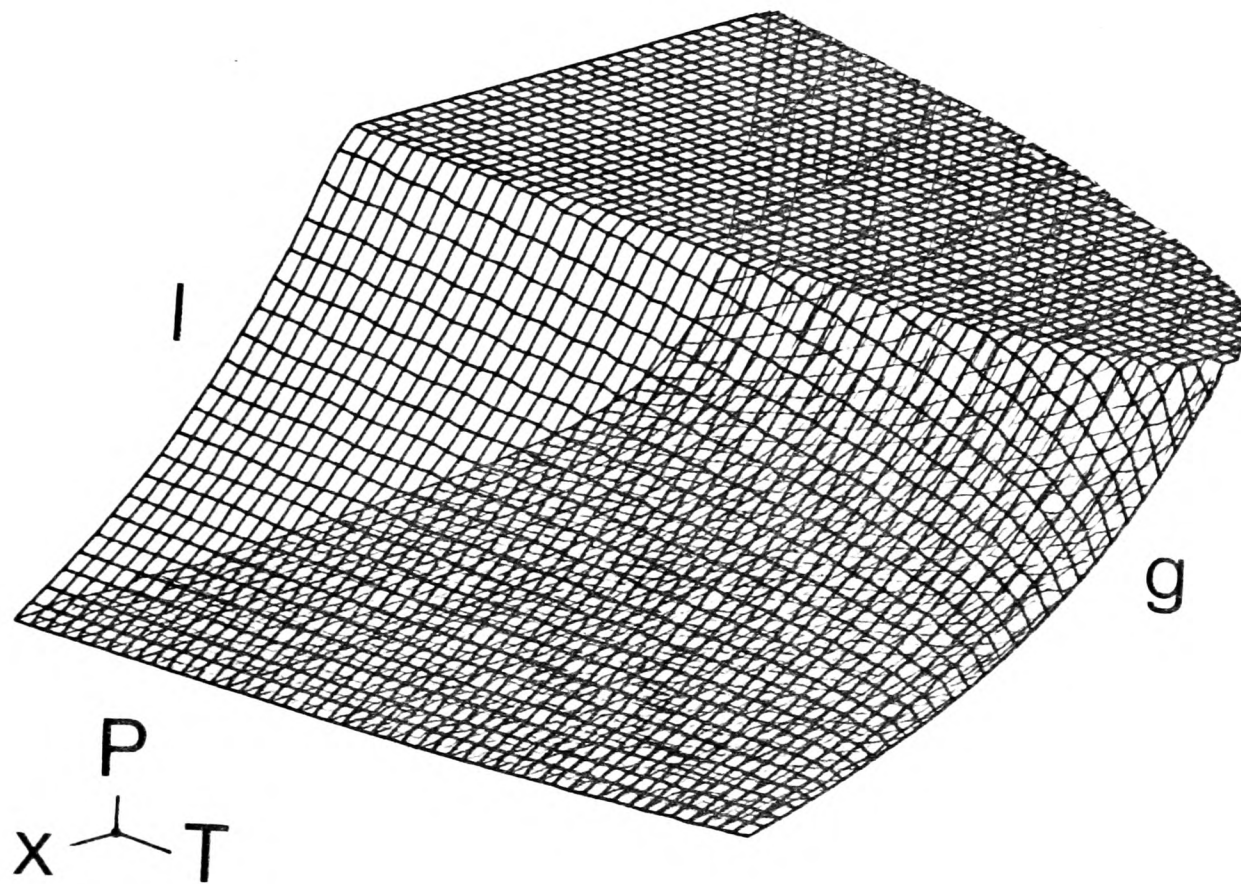
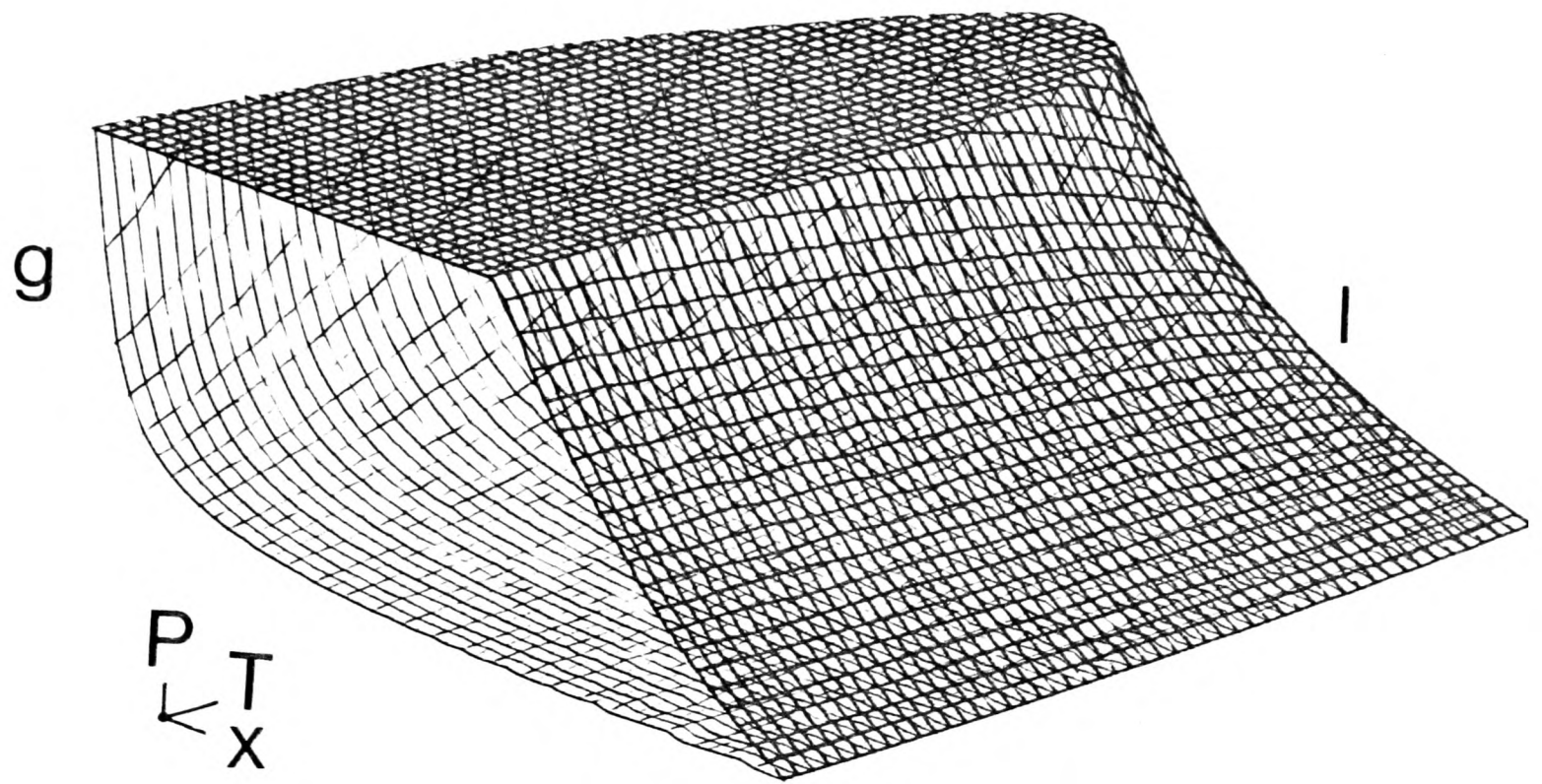


Fig. 4.10 Pressure-temperature-composition PTx surface for a mixture of points and hard cores with $a_{11}=0$ and $a_{12}=0$.

4.8.2 System With $a_{11}=0$, $a_{12}=a_{22}/2$ And $a_{22}>0$

The system of interest is a binary mixture of points and hard cores with no attractive interactions between the points and with the point-sphere interactions taken as the arithmetic mean of the pure attractions.

$$a_{11} = 0, \quad a_{12} = (a_{11} + a_{22})/2 = a_{22}/2, \quad a_{22} > 0$$

As before the mixture's temperature and pressure are reduced with respect to the temperature and pressure of the pure hard core system.

$$P_r = \frac{\eta(1+\eta(3x_2-2)+\eta^2-\eta^3x_2)T_r}{\eta_{c,2}Z_{c,2}x_2(1-\eta)^3} - \frac{A_{c,2}\eta^2}{\eta_{c,2}Z_{c,2}x_2}$$

4.8.2.1 The Critical Lines -

This particular choice of attractive interactions considerably simplifies the expressions for the mixed derivatives of the free energy with respect to volume and composition, and the corresponding conditions for a critical point are more easily determined (Section 4.6). The two conditions that must be satisfied at a critical point are expressed in terms of the reduced critical density η_c , the critical composition x of the spheres ($x=x_2$), and a parameter A_c which is an appropriate function of temperature.

The first condition can be written

$$A_{2v}A_{2x} - A_{vx}^2 = 0$$

$$\frac{\eta_c^4 R^2 T_c^2}{x^4 b^2} \left[A_c^2 + \frac{2A_c(x - \eta_c)}{(1-x)\eta_c(1-\eta_c)} + x \frac{(-1 - 4\eta_c - 4\eta_c^2 + 4\eta_c^3 - \eta_c^4)}{(1-x)\eta_c^2(1-\eta_c)^4} \right] = 0$$

$$A_c = \frac{a_{22}}{RT_c b}, \quad b = \pi L d_2^3 / 6$$

The second condition is

$$A_{3v}A_{2x}^2 - 3A_{2vx}A_{vx}A_{2x} + 3A_{v2x}A_{vx}^2 - A_{3x}A_{2v}A_{vx} = 0$$

$$\begin{aligned} & A_o^2 \left[\begin{aligned} & (-4x^3 + 8x^2 - 4x - 2)\eta_o^7 + (20x^3 - 46x^2 + 32x + 4)\eta_o^6 \\ & + (-22x^3 + 62x^2 - 58x - 2)\eta_o^5 + (-36x^3 + 52x^2 + 4x)\eta_o^4 \\ & + (18x^3 - 26x^2 - 2x)\eta_o^3 + (-2x^2 + 4x)\eta_o^2 \end{aligned} \right] \\ & + \frac{A_o}{(1-\eta_o)} \left[\begin{aligned} & (-12x^2 + 9x + 6)\eta_o^7 + (8x^3 + 56x^2 - 70x - 14)\eta_o^6 \\ & + (-40x^3 - 34x^2 + 125x + 10)\eta_o^5 + (44x^3 - 166x^2 + 8x - 2)\eta_o^4 \\ & + (72x^3 + 58x^2 - 11x)\eta_o^3 + (-36x^3 - 2x^2 - 14x)\eta_o^2 + (4x^2 + x)\eta_o \end{aligned} \right] \\ & + \frac{x}{(1-\eta_o)^4} \left[\begin{aligned} & (-4x^2 + 3x + 2)\eta_o^9 + (36x^2 - 35x - 11)\eta_o^8 + (-118x^2 + 143x + 23)\eta_o^7 \\ & + (116x^2 - 233x - 29)\eta_o^6 + (150x^2 + 71x + 37)\eta_o^5 + (-284x^2 + 95x - 31)\eta_o^4 \\ & + (-94x^2 + 115x + 3)\eta_o^3 + (36x^2 + 3x + 7)\eta_o^2 + (18x^2 - 16x - 1)\eta_o - 2x \end{aligned} \right] \\ & = 0 \end{aligned}$$

The following factor multiplying the above expression has been omitted:

$$R^3 T_c^3 \eta_c^3 / [x^7 b^3 (1-x)^2 (1-\eta_c)^5]$$

Before these expressions are solved for the critical points at various compositions, it is instructive to examine the limiting form of the equations when the mole fraction is one, corresponding to pure hard cores, and when the mole fraction is zero, corresponding to pure points. In the case of a mole fraction of one, the two conditions can be expressed as

$$\underline{x = 1}$$

$$2A_c/\eta_c + \frac{(-1-4\eta_c-4\eta_c^2+4\eta_c^3-\eta_c^4)}{\eta_c^2(1-\eta_c)^4} = 0$$

$$A_c^2(-2\eta_c^7+10\eta_c^6-20\eta_c^5+20\eta_c^4-10\eta_c^3+2\eta_c^2)$$

$$+A_c(3\eta_c^7-20\eta_c^6+61\eta_c^5-116\eta_c^4+119\eta_c^3-52\eta_c^2+5\eta_c)/(1-\eta_c)$$

$$+(\eta_c^9-10\eta_c^8+48\eta_c^7-146\eta_c^6+258\eta_c^5-220\eta_c^4+24\eta_c^3+46\eta_c^2+\eta_c-2)/(1-\eta_c)^4 = 0$$

These two equations can be solved for η_c and A_c , and the following roots are obtained:

$$\eta_c = 0.130444, \quad A_c = 10.6012, \quad \eta_c = 1, \quad A_c = \infty$$

As expected the results determined in Chapter 3 for the pure hard core system are obtained when the conditions for a critical point are solved simultaneously at $x_2=1$. The other root represents the end point of another critical line, as

will become clear later.

The conditions for critical points at a mole fraction of zero are simply

$$\underline{x = 0}$$

$$A_c \eta_c^4 [A_c - 2 / (1 - \eta_c)] = 0$$

$$A_c \eta_c^4 (1 - \eta_c) [-2 (1 - \eta_c) A_c \eta_c + (6 \eta_c - 2)] = 0$$

the roots are

$$\eta_c = 0, A_c = 2, \eta_c = 1, A_c = \infty$$

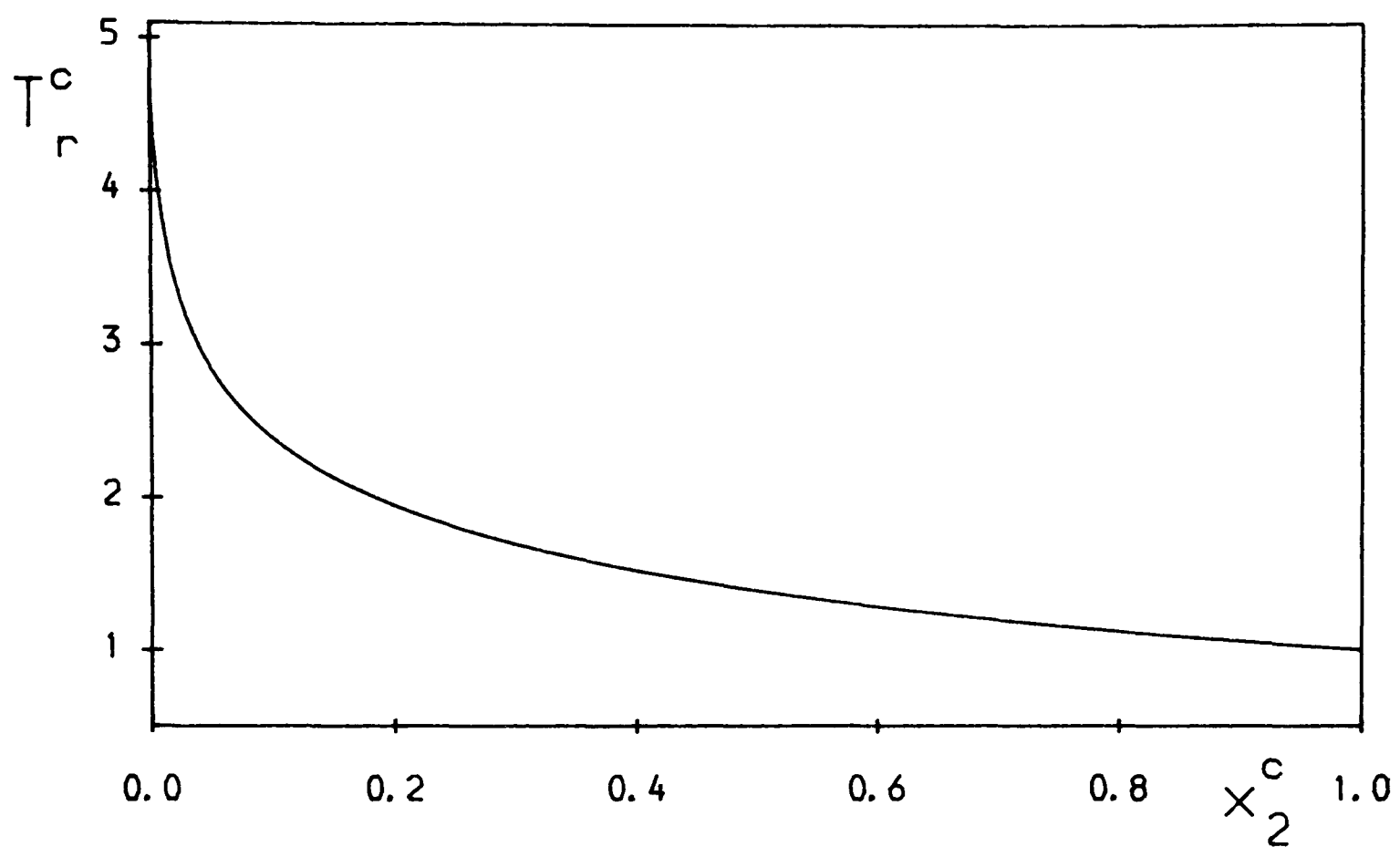
and their significance will be discussed.

The critical points at other values of the composition are obtained by solving the two conditions for critical points as described in Section 4.6. After eliminating A_c and factorising the resulting expression, a 16th order polynomial in reduced critical density is obtained which is solved numerically at varying mole fractions. Two critical lines emerged from these calculations. The lines are represented graphically by plotting the reduced critical temperature, pressure and densities for each component versus the corresponding value of the composition at the critical point. It must be kept in mind that the temperature, pressure and density are reduced with respect to a system of pure hard spheres (see Chapter 3).

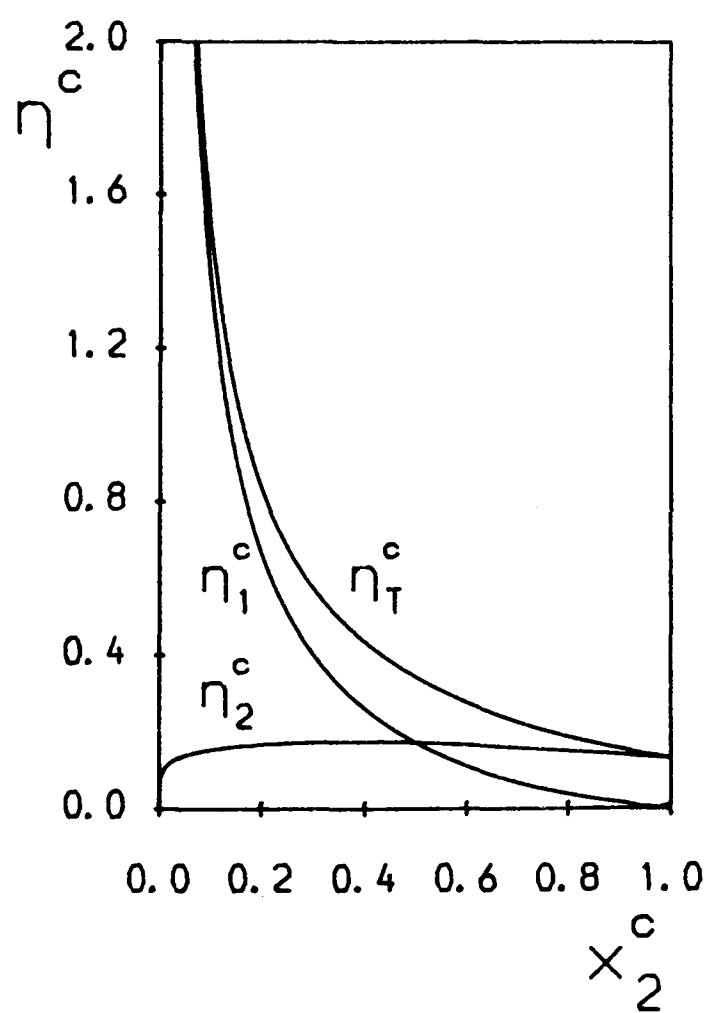
For the gas-liquid critical line, the reduced critical temperature varies with composition as seen in Fig. 4.11(a). Fig. 4.11(b-c) show the variations of the reduced critical density (η_1^C for species 1, η_2^C for species 2, and η_T^C for the total number density) and reduced critical pressure with respect to composition. An investigation of the mixture's pressure-composition phase diagrams will confirm that this critical line represents the loci of gas-liquid critical points for our system of point particles and hard cores.

The critical line shows an increase in the critical temperature, with respect to the critical temperature of pure hard cores (component 2), as the mole fraction x_2 of component 2 decreases. This suggests that the point particles are enhancing the system's attractive interactions. The fact that the reduced critical density for component 1 (points) increases sharply with decreasing hard core mole fraction is consistent with this "glue" effect.

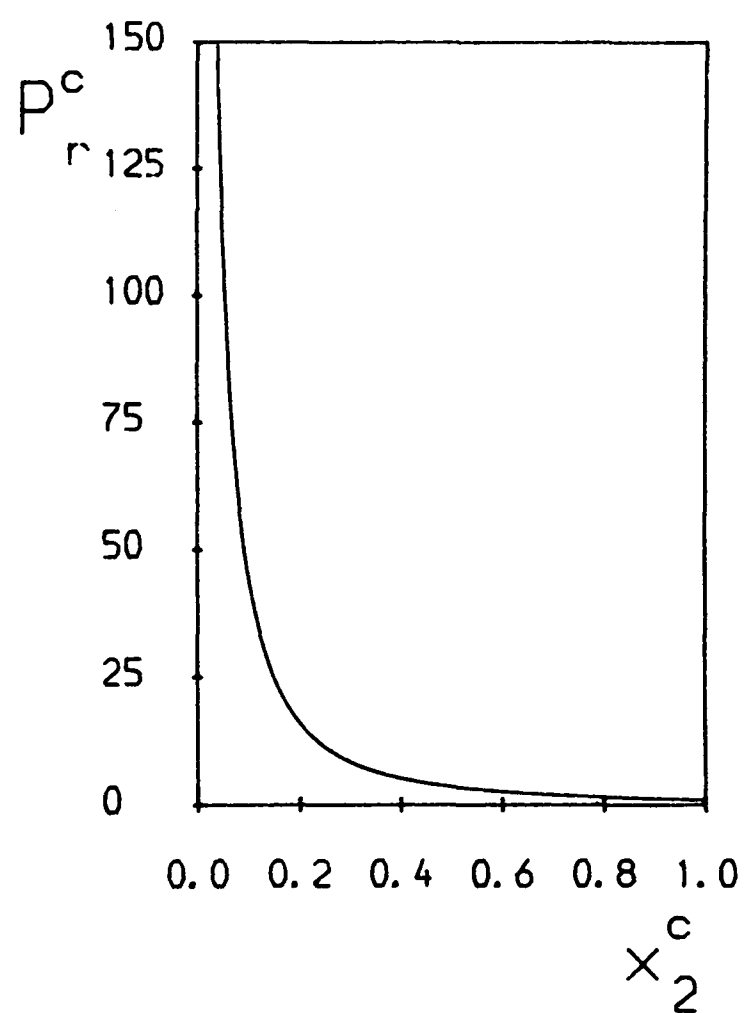
Another very interesting feature of the critical line is that it appears to have a limiting critical temperature at a hard core composition of zero. When the conditions for critical points are solved for $x_2=0$, a value of $A_C=2.0$ is obtained corresponding to a reduced critical temperature of $T_r=5.3006=10.6012/2$. The critical pressure tends to infinity as this point is reached. This strange limiting behaviour seems to be forced on the system by setting the diameter of one of the spheres as infinitely small.



(a)



(b)



(c)

Fig. 4.11 The gas-liquid critical line for a mixture of hard cores and point particles with $a_{11}=0$ and $a_{12}=a_{22}/2$.

A plausible hypothesis is that, as the solution becomes infinitely dilute, the points are drawn towards the surface of the remaining spheres with the pressure becoming infinite. Above the limiting temperature the repulsive kinetic forces are sufficiently strong to counteract the attractive forces.

A comparison of this system's gas-liquid critical line with the critical line obtained in Section 4.8.1.1 for a mixture of points and hard cores with $a_{12}=0$ is provided graphically in Fig. 4.12.

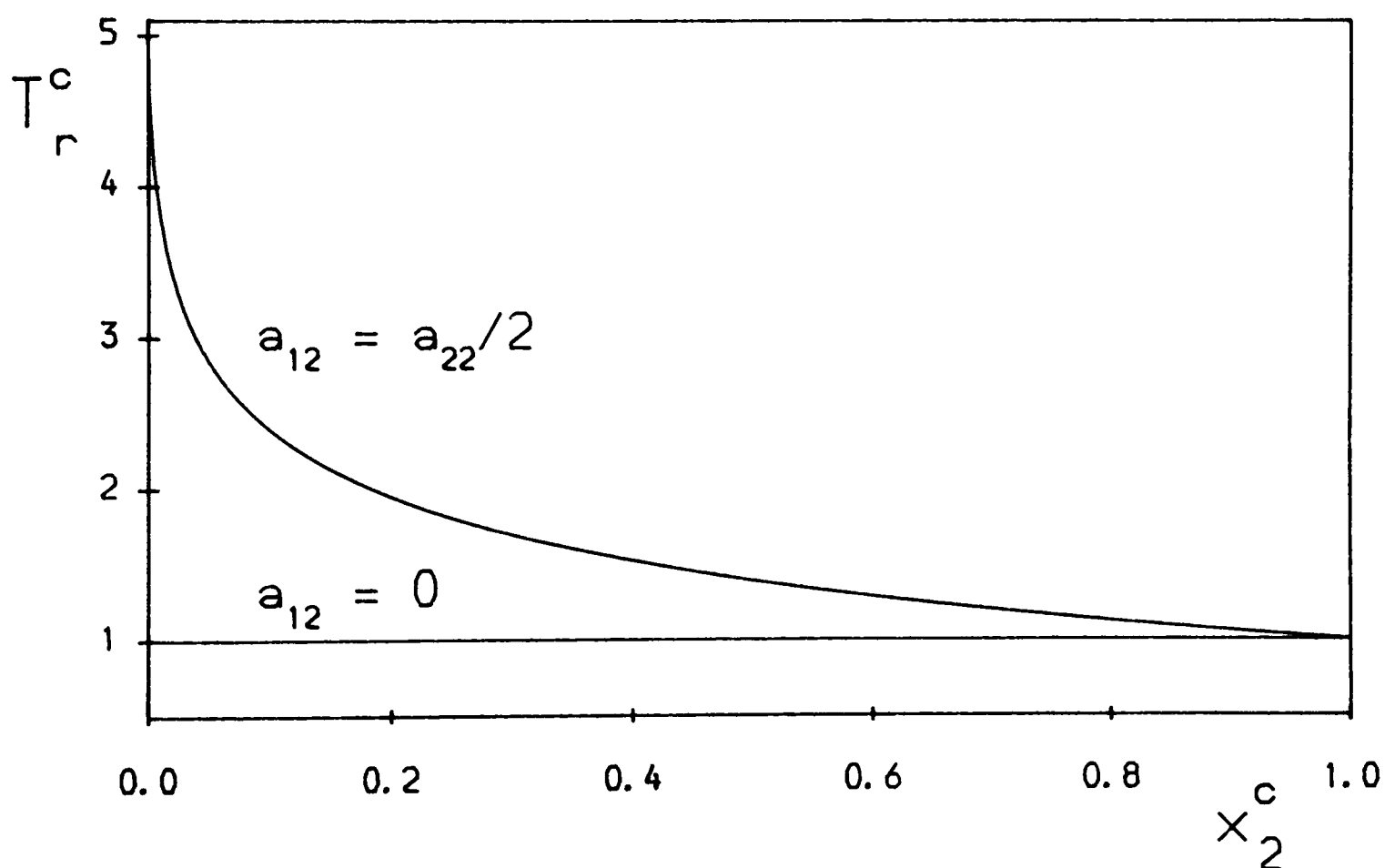


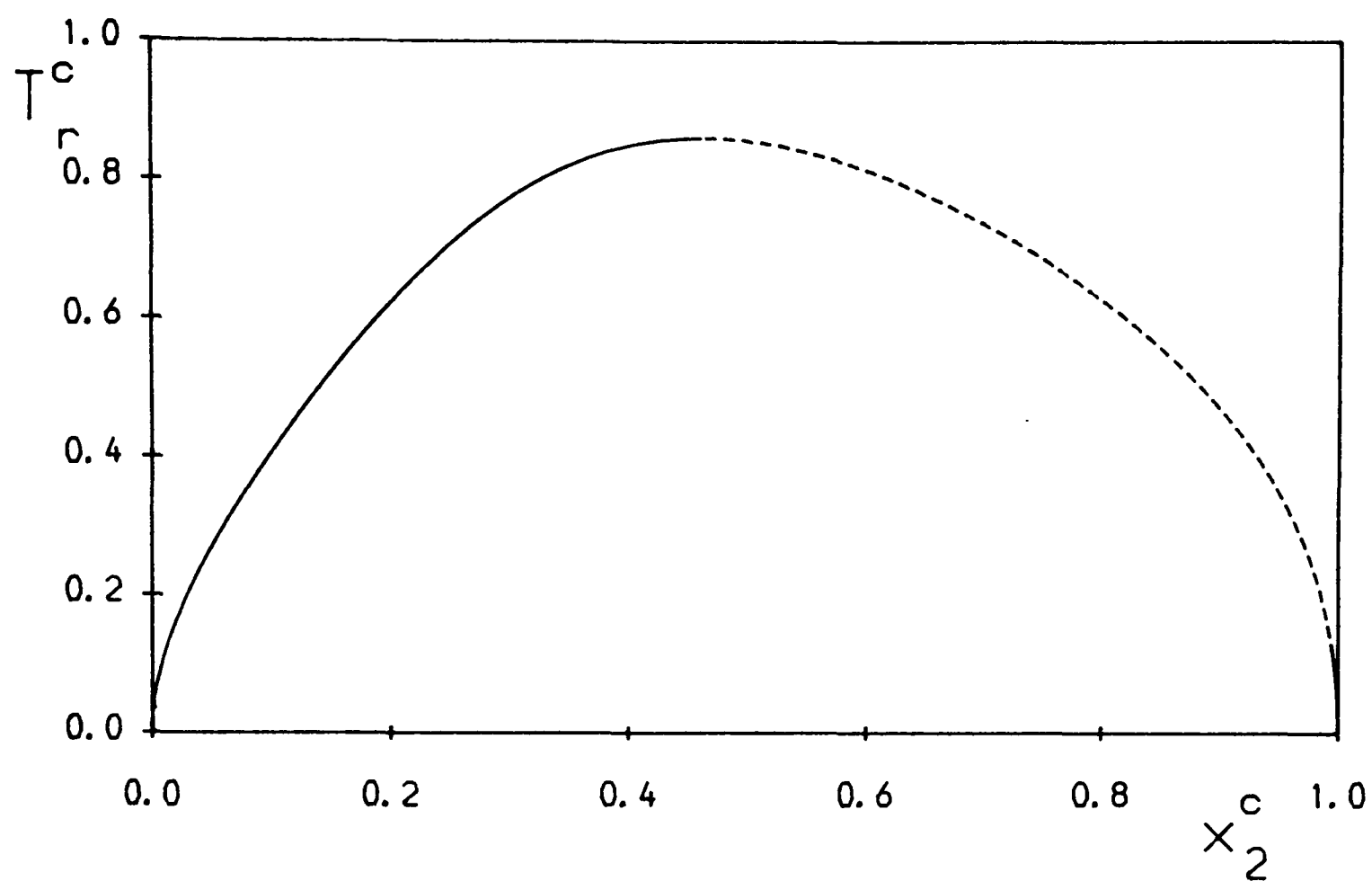
Fig. 4.12 The temperature-composition representation of the gas-liquid critical line for the system without point-sphere attractive interactions ($a_{12}=0$) is compared with the results for $a_{12}=a_{22}/2$.

The second critical line obtained in the calculations is associated with liquid-liquid critical points. The reduced critical temperature, pressure and densities are plotted against composition in Fig. 4.13(a-c) with the unstable portions of the lines shown as dashed.

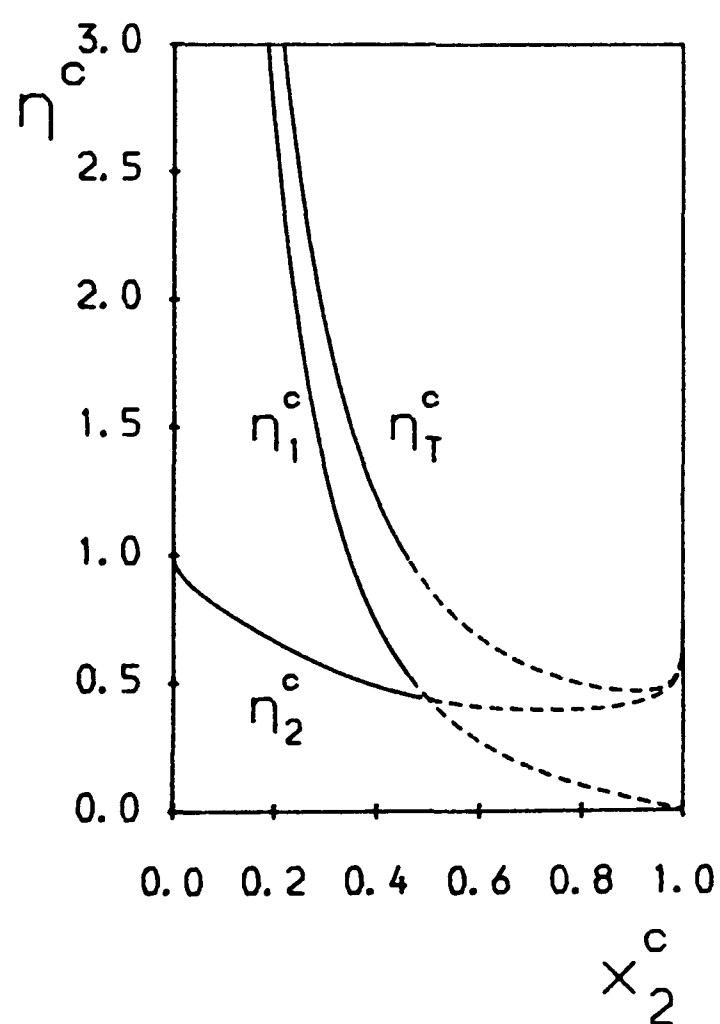
As the mole fraction of the hard cores approaches zero, the reduced critical temperature tends to zero with a corresponding critical pressure of infinity. Although the pressure becomes negative for compositions above $x_2=0.3086$, the critical line becomes metastable before this point by meeting a three phase liquid-liquid-gas line at an upper critical end point (UCEP) as shown in Section 4.8.2.2.

The instability (as distinct from metastability) of a critical line can be established by numerically determining the sign of the fourth derivative of the Gibbs free energy with respect to composition using a computer; negative values of the derivative represent instability. In the case of the liquid-liquid critical line, the onset of instability corresponds to the point where the temperature-composition and pressure-composition curves simultaneously reach a maximum, and this occurs at a negative pressure with $x_2=0.4608$. The critical line's metastability is established from a study of the pressure-composition phase diagrams in the next section.

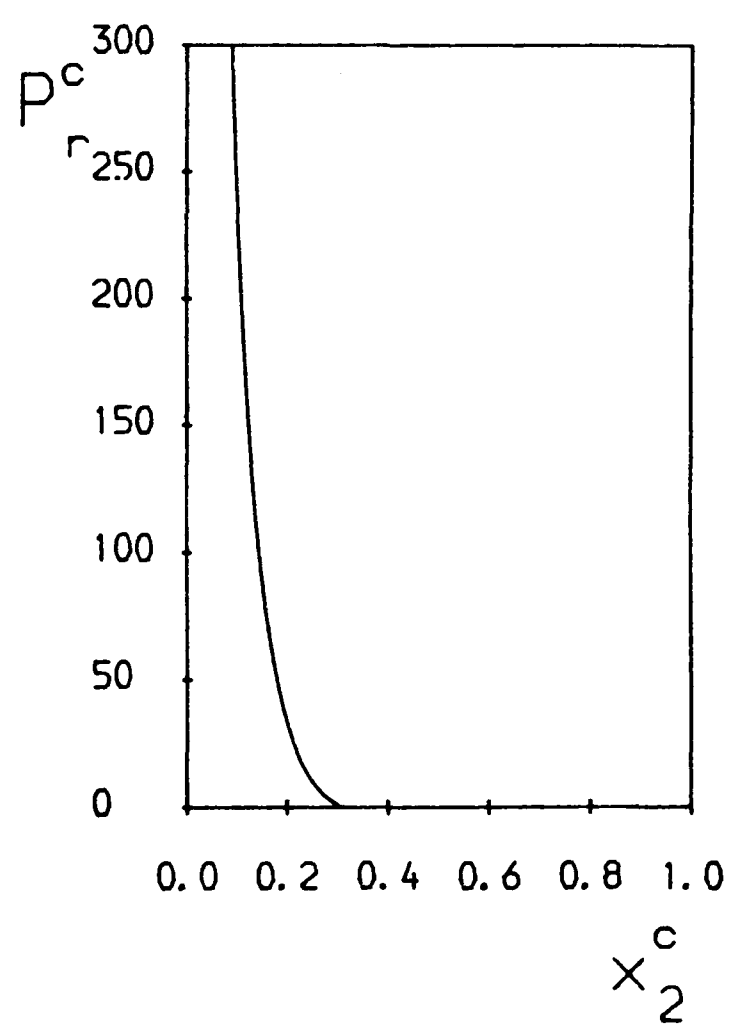
Similar gas-liquid and liquid-liquid critical lines are obtained for mixtures of points and van der Waals molecules with the same attractive interactions in Chapter 6.



(a)



(b)



(c)

Fig. 4.13 The liquid-liquid critical line for a mixture of hard cores and point particles with $a_{11}=0$ and $a_{12}=a_{22}/2$.

4.8.2.2 Pressure-Composition Phase Diagrams -

The behaviour of the gas-liquid and surprising liquid-liquid critical lines is more clearly understood after an investigation of the corresponding pressure-temperature-composition, PTx, surface. The phase behaviour of a binary mixture can be conveniently described by using pressure-composition, Px, constant-temperature slices of the PTx surface. To establish the details of the Px phase diagram it becomes necessary to use all the conditions applicable to the coexistence of two phases.

$$p^{\alpha} = p^{\beta}, \quad T^{\alpha} = T^{\beta}, \quad \mu_1^{\alpha} = \mu_1^{\beta}, \quad \mu_2^{\alpha} = \mu_2^{\beta}$$

The chemical potentials expressed as the logarithm of the activities are obtained from Section 4.5.

$$\ln \lambda_1 = (\mu_1 - \mu_1^{\bullet}) / RT = \ln(\eta) + \ln[(1-x_2)/x_2] - \ln(1-\eta) - A_c \eta / T_r$$

$$\ln \lambda_2 = (\mu_2 - \mu_2^{\bullet}) / RT = \ln(\eta) + \frac{(1-x_2)\eta}{x_2(1-\eta)} + \frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3} - \frac{(1+x_2)A_c\eta}{x_2 T_r}$$

where λ_1 and λ_2 are the activities established with respect to a standard state corresponding to the ideal gas at the molar hard sphere volume b with

$$b = \pi L d_2^3 / 6, \quad \mu_i^{\bullet} = -RT \ln[(2\pi m_i kT / h^2)^{3/2} b / L]$$

The equation of state is restated in its reduced form as

$$P_r = \frac{\eta (1 + \eta (3x_2 - 2) + \eta^2 - \eta^3 x_2) T_r}{\eta_{c,2} Z_{c,2} x_2 (1 - \eta)^3} - \frac{A_{c,2} \eta^2}{\eta_{c,2} Z_{c,2} x_2}$$

For a mixture at constant temperature and pressure, the compositions of the coexisting phases can be determined from the system's activity plots.

By solving the equation of state as described in Section 4.7, the logarithm of the activities of component 1 are plotted against those of component 2 for the gas and liquid roots. A computer program is then used to determine the points of intersection so that the compositions and densities for phase equilibrium are established at a given temperature and pressure. By varying the pressure and repeating the former procedure, the complete pressure-composition phase diagram is obtained as a fixed temperature slice of the PTx surface.

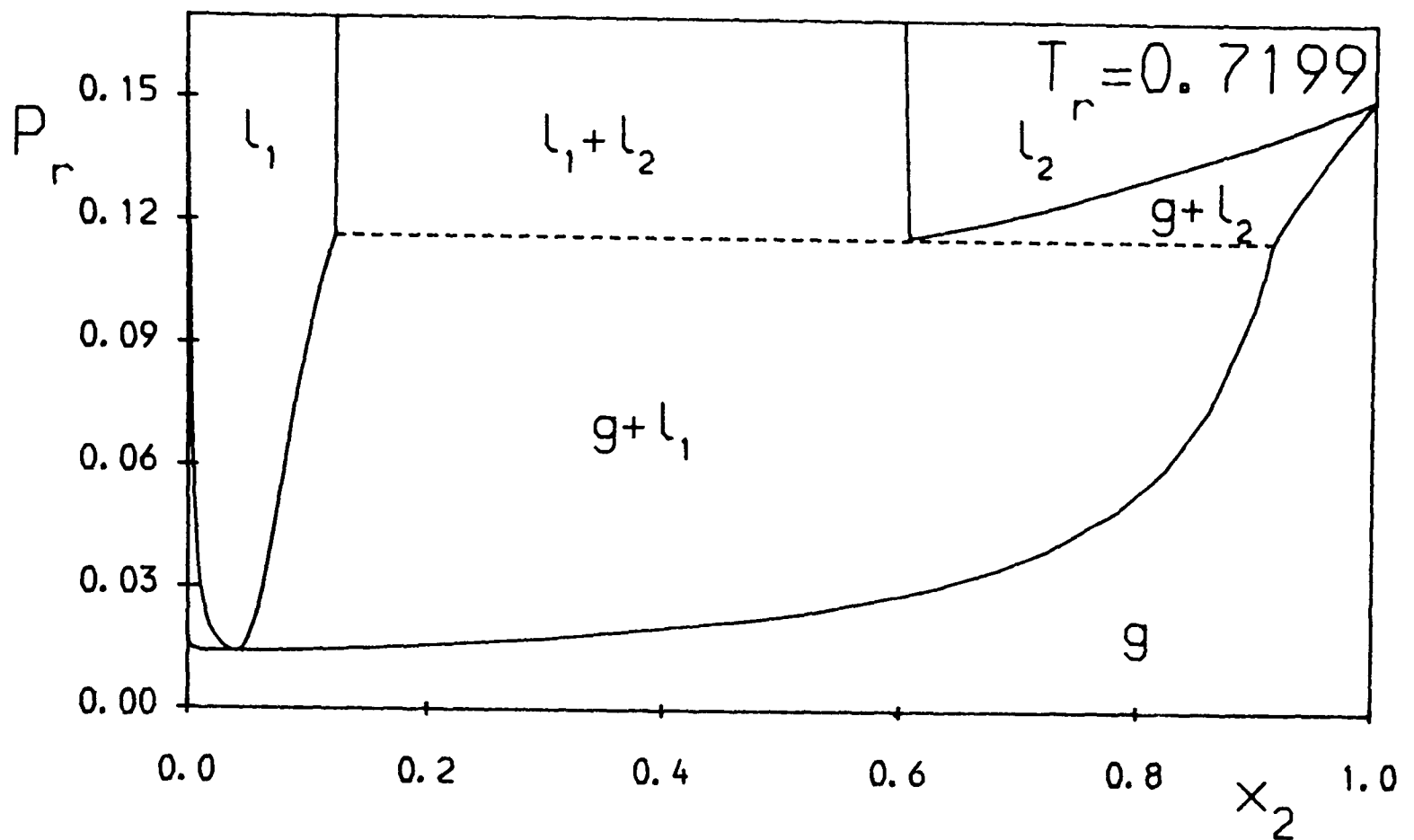
The corresponding Px phase diagrams are represented in Fig. 4.14(a-e). At a reduced temperature of $T_r = 0.7199$, below the critical temperature for the pure hard core system, gas-liquid and liquid-liquid phase coexistence is seen with liquid-liquid-gas three phase coexistence at a fixed temperature and pressure (dashed line in Fig. 4.14(a)). As the composition becomes zero the pressure tends to infinity due to the limit $d_1 = 0$ and $a_{11} = 0$. The negative azeotrope appearing at a low

composition ($x_2=0.0142$) is presumably a result of this unusual limiting behaviour. The liquid-liquid immiscibility disappears at much higher pressures; the liquid-liquid critical point is at a reduced pressure of $P_r=8.15$ and due to scaling problems it is not shown on the phase diagram.

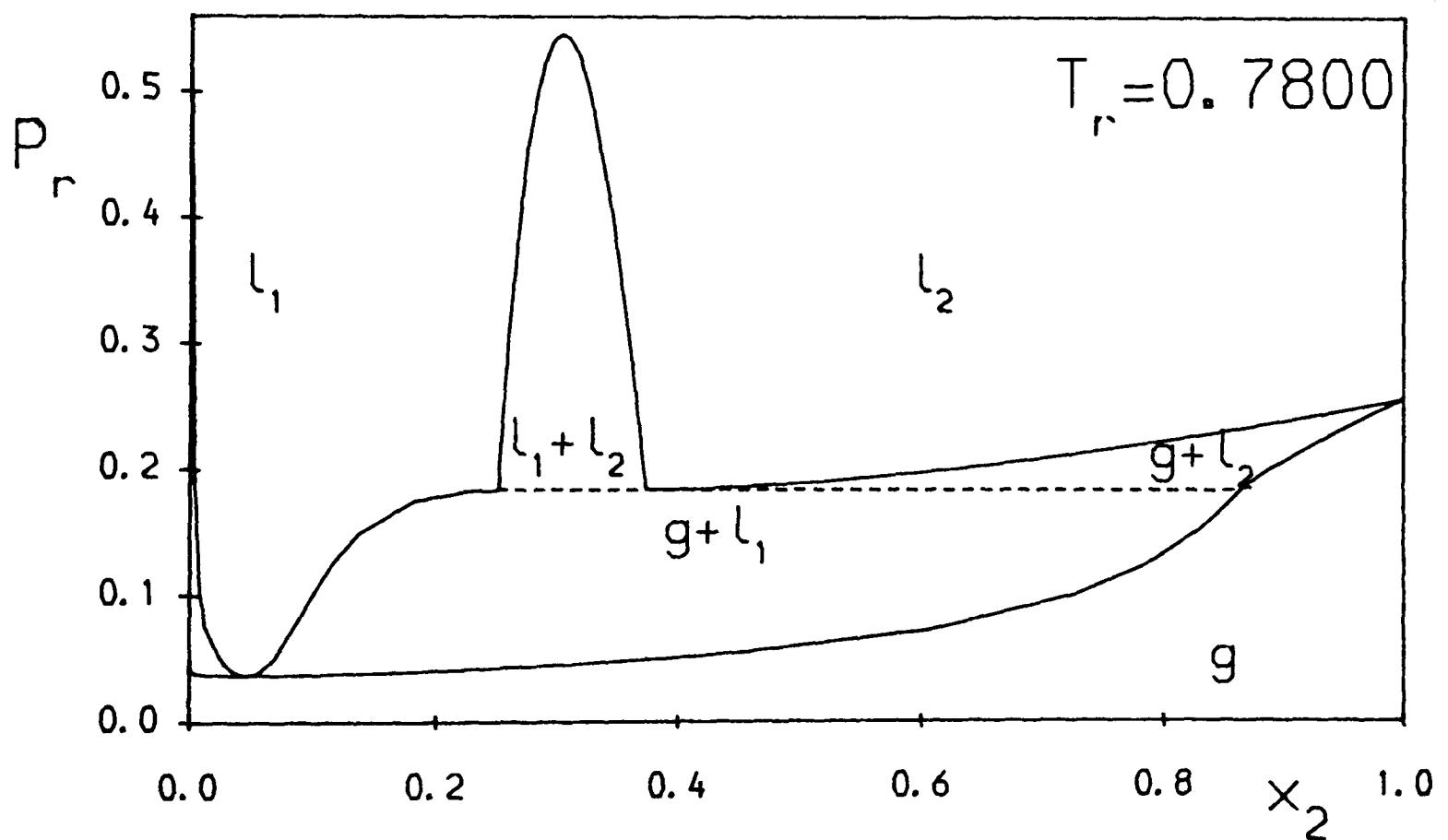
As the temperature is increased the value of the liquid-liquid critical pressure decreases (see Fig. 4.14(b) for a reduced temperature of $T_r=0.7800$) and the critical point finally disappears at an upper critical end point beyond which only gas-liquid equilibrium is seen. Fig. 4.14(c) represents the P_x phase diagram at a temperature of $T_r=0.8746$ which is above the upper critical end point.

Gas-liquid critical points appear above a reduced temperature of $T_r=1.0$ (see Fig. 4.14(d-e)), corresponding to the appropriate points on the gas-liquid critical line. This behaviour implies "gas-gas immiscibility" with the mixture phase separating at temperatures above the critical temperature of the pure hard core system. As the temperature is increased even further, the azeotrope eventually cuts into the gas-liquid critical line.

These features of the PT_x surface's phase behaviour are summarized on a pressure-temperature projection in Section 4.8.2.3.

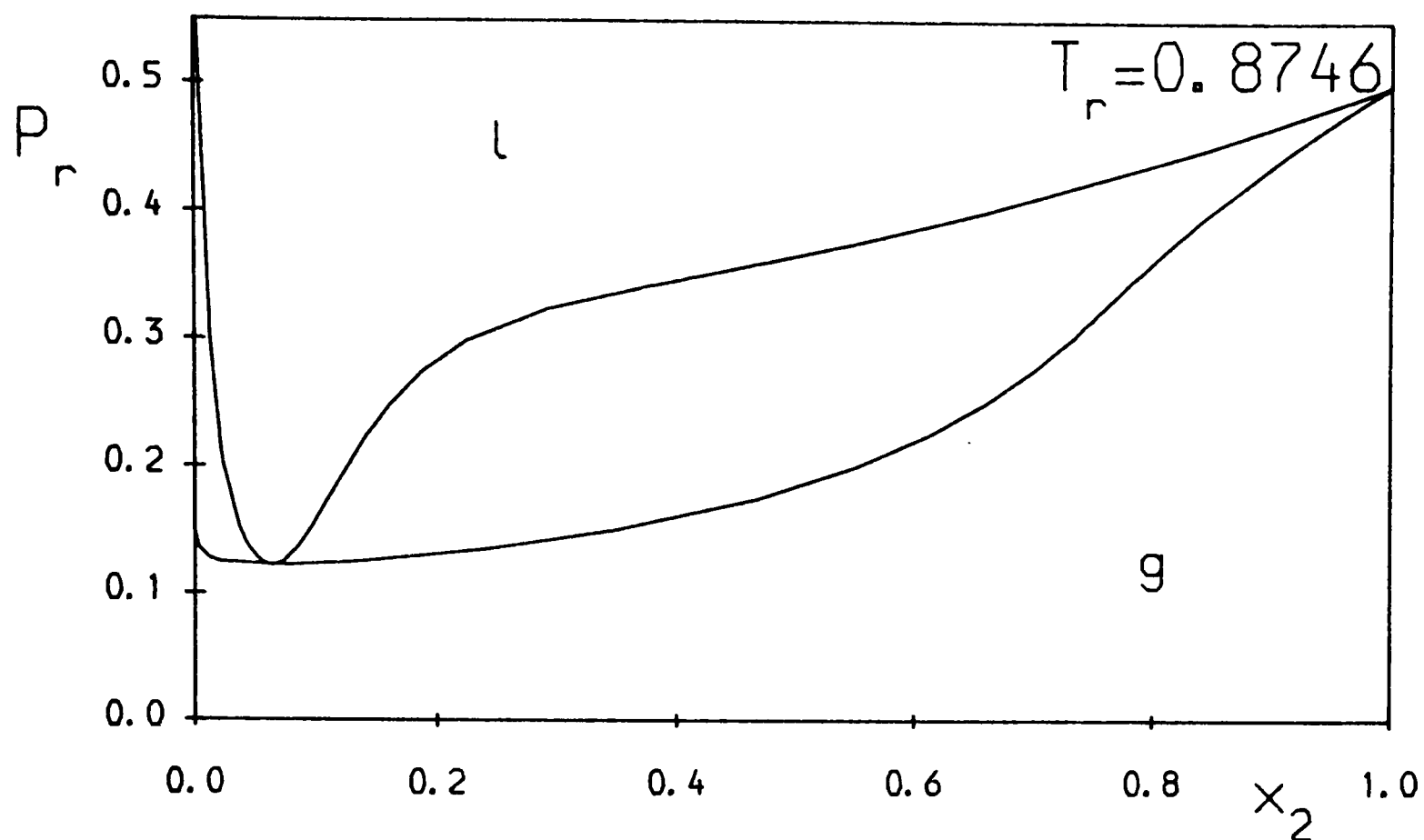


(a)

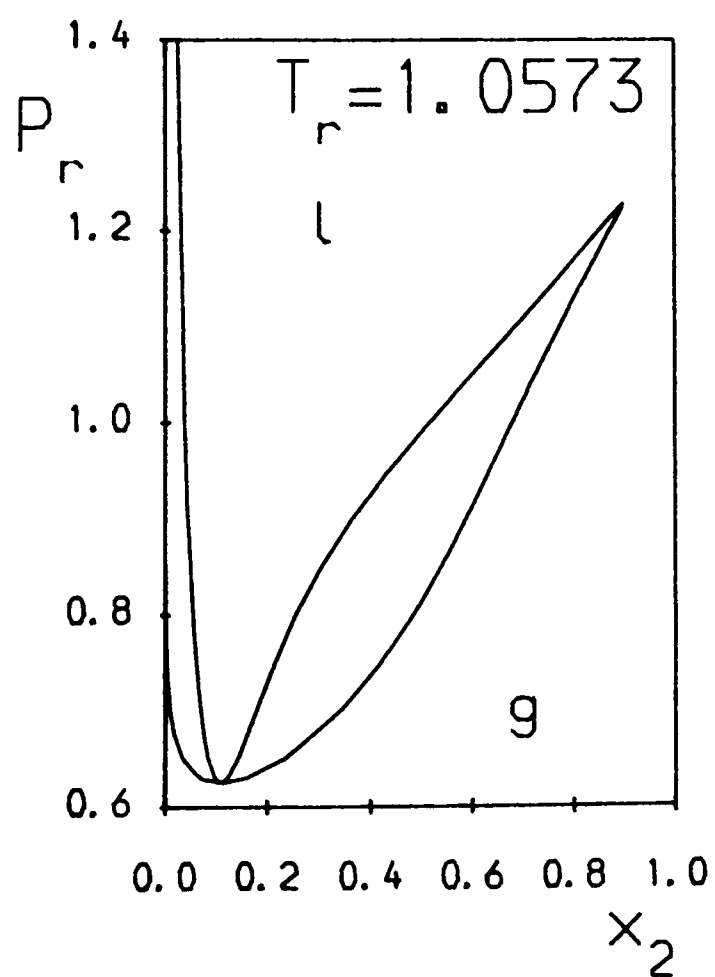


(b)

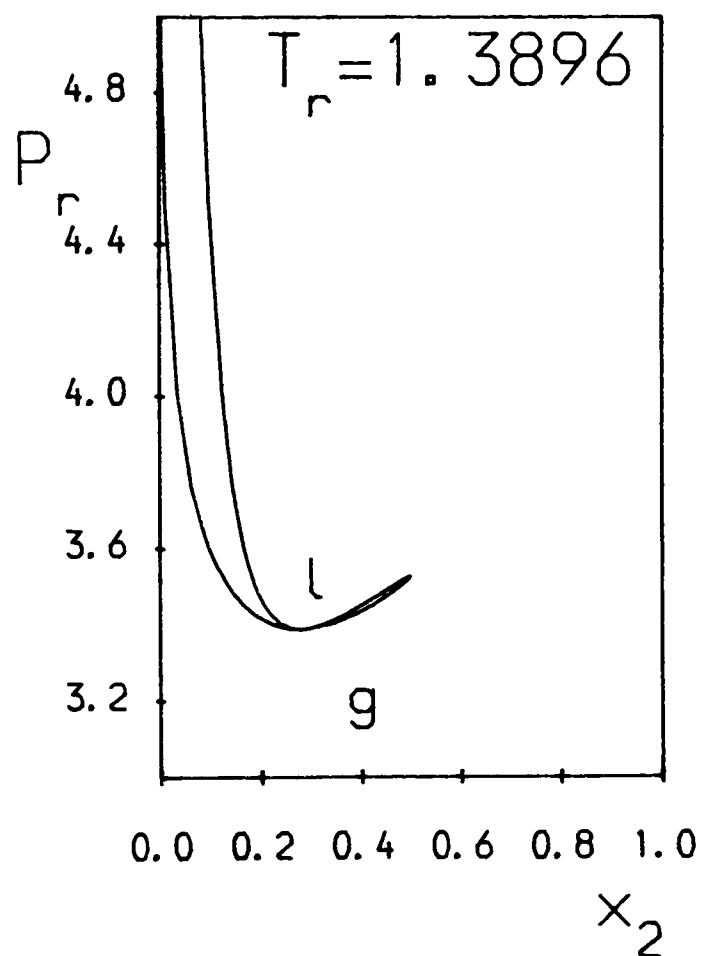
Fig. 4.14 Isothermal pressure-composition phase diagrams for a point-hard core mixture with $a_{11}=0$ and $a_{12}=a_{22}/2$.



(c)



(d)



(e)

 Fig. 4.14(cont'd) Pressure-composition phase diagrams for a point-hard core mixture with $a_{11}=0$ and $a_{12}=a_{22}/2$.

4.8.2.3 Pressure-Temperature Projection -

The pressure-temperature PT projection of the PTx surface for the point-hard core mixture is shown on Fig. 4.15(a); the vapour pressure curve for the pure hard core system is the solid line (2), the azeotropic line is labelled (AZ), the liquid-liquid-gas coexistence line is denoted l_1l_2g , and the PT projections of the two critical lines are shown dotted.

An increase in temperature along the gas-liquid critical line results in an increase in the critical pressure so that the slope of the line remains positive at all times. Scott [54] has referred to this kind of behaviour as "gas-gas immiscibility of the first kind". Fig. 4.15(b) shows the limiting behaviour of the gas-liquid critical line which becomes asymptotic to the isotherm $T_r=5.3006$ as the pressure tends to infinity. The liquid-liquid critical line ends at an upper critical end point (UCEP) when it meets the three phase line at a reduced temperature of $T_r=0.7841$ and a reduced pressure of $P_r=0.1886$. At very high pressures the liquid-liquid critical temperature and composition tend to zero as the pressure is increased.

The results obtained for this system of point particles and hard cores suggest that two opposing effects are influencing the phase diagrams. Although the points seem to be binding the spheres together, resulting in an increase of the gas-liquid critical temperature, there is also an indication of repulsive interactions in regions of the phase diagram associated with the liquid-liquid immiscibility.

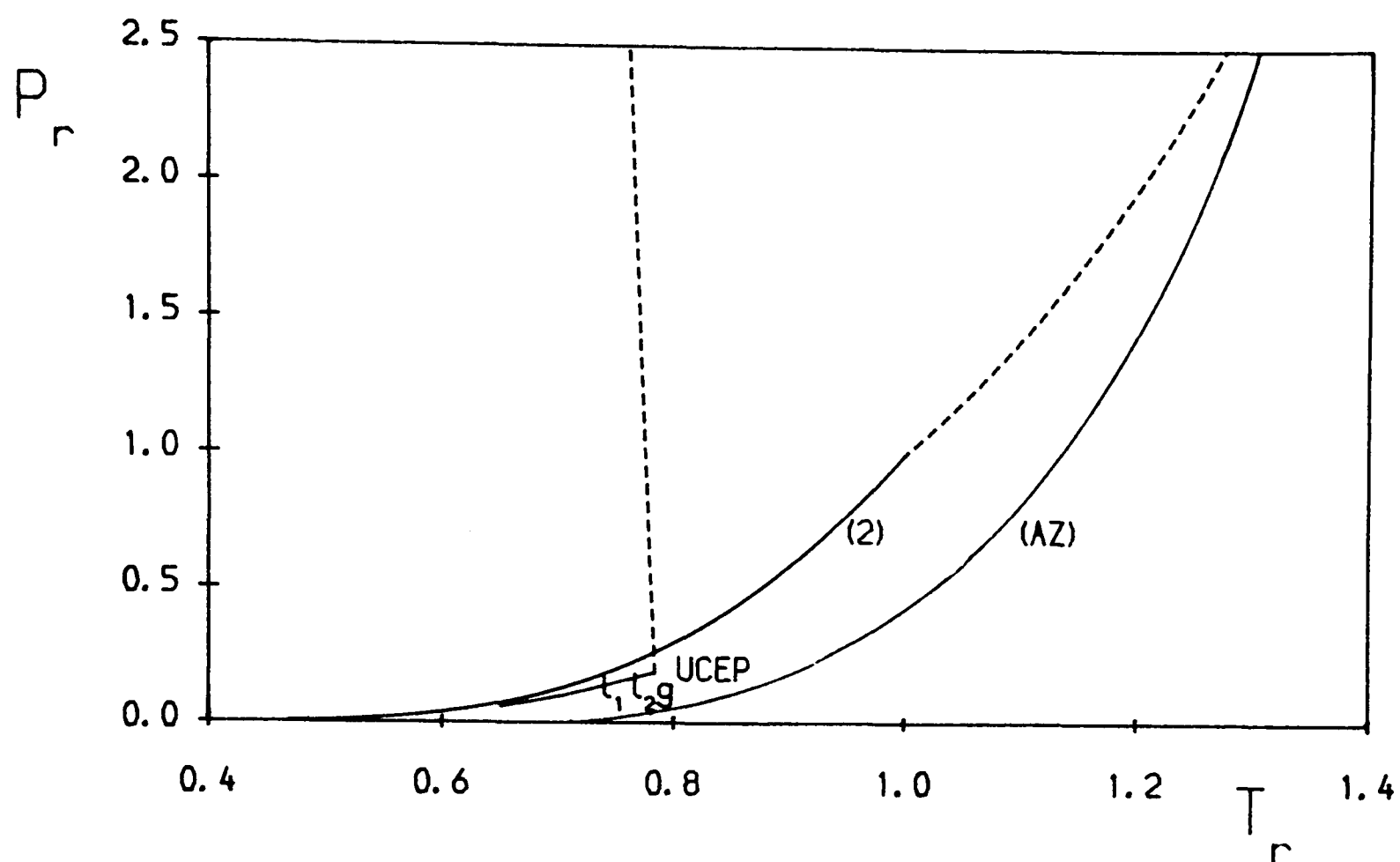


Fig. 4.15(a) The pressure-temperature projection for the point-hard core mixture with $a_{11}=0$ and $a_{12}=a_{22}/2$.

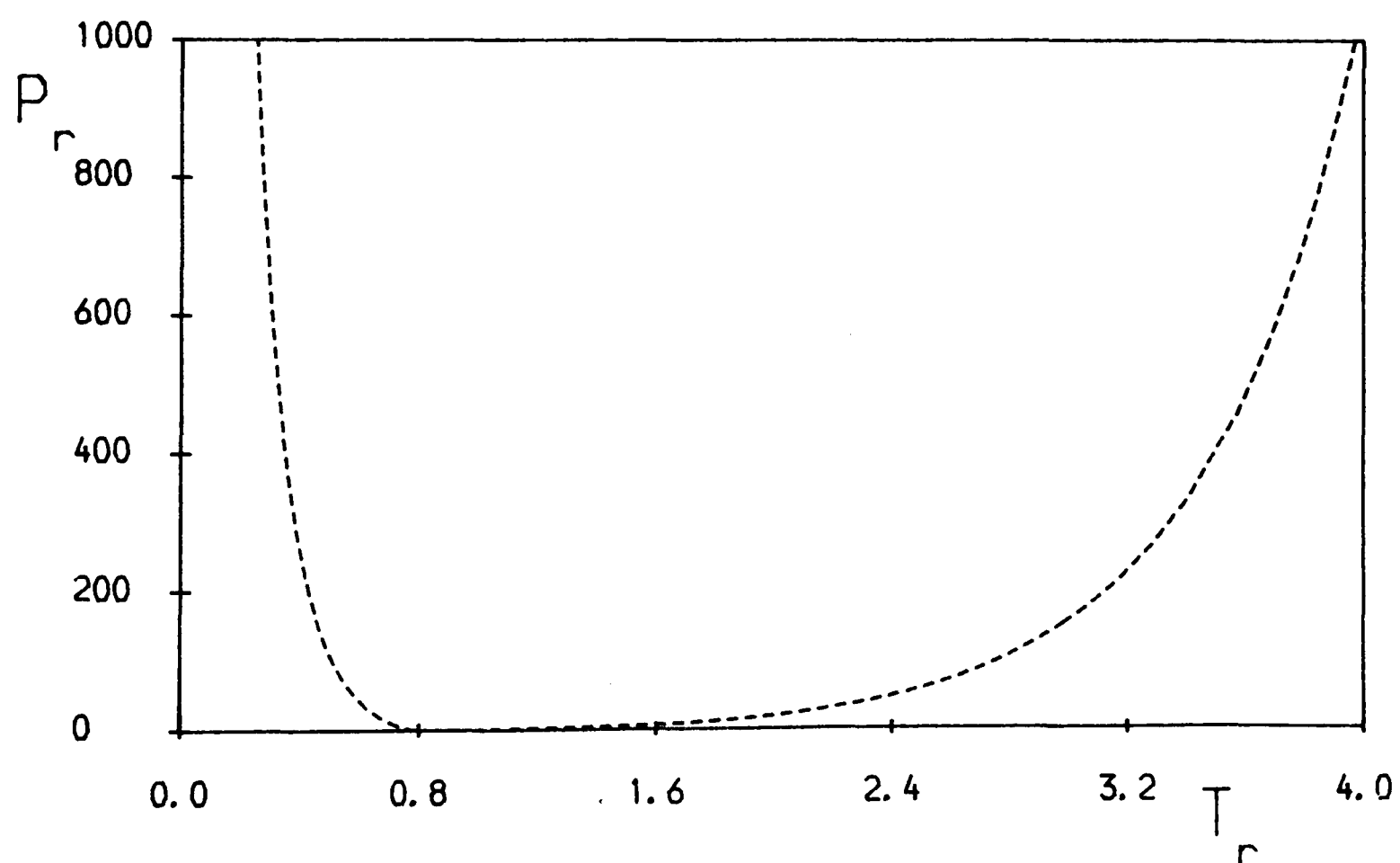


Fig. 4.15(b) The PT limiting behaviour of the critical lines.

4.8.2.4 Temperature-Density Projection -

The final phase diagram examined for the mixture with $a_{12}=a_{22}/2$ is the temperature-density projection. An investigation of the PT projection indicated that the liquid-liquid-gas line ends at an UCEP, and as this point is approached, the compositions and densities of the two liquid phases become identical.

Fig. 4.16 shows the gas and liquid reduced densities at various temperatures along the three phase line. The densities of the two liquid phases become identical at the UCEP corresponding to a reduced temperature of $T_r=0.7841$ and a reduced density of $\eta_2^l=0.5559$. The coexisting gas phase appears at much lower reduced densities with a value of $\eta_2^g=0.0109$ at the UCEP.

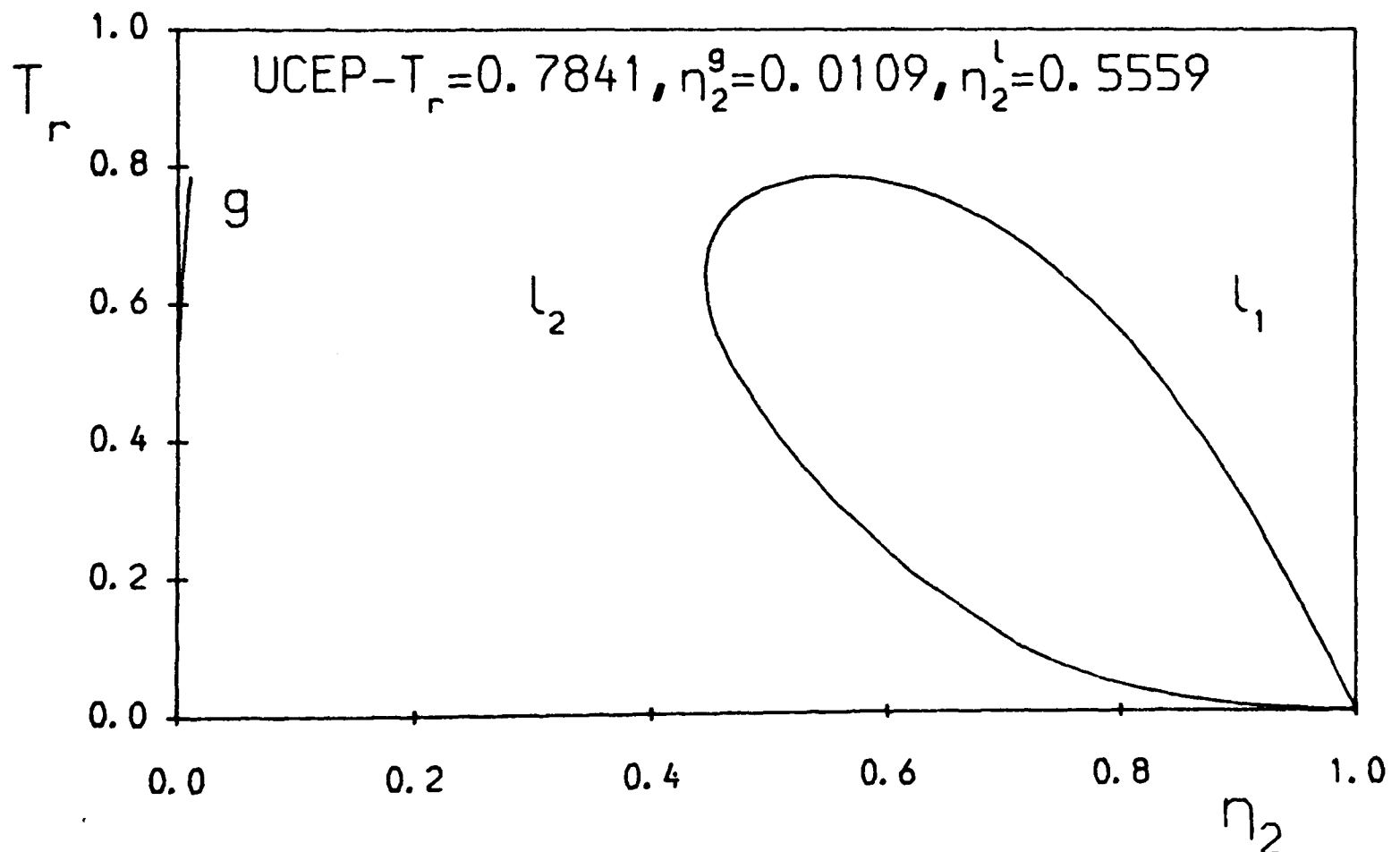


Fig. 4.16 Temperature-density projection for the liquid and gas densities along the three phase line.

An unusual feature of the phase diagram is the curving back of the less dense liquid densities at lower temperatures so that both liquid phases have a zero temperature limit for the reduced density of 1.0. This limiting value means that the number density, N/V for l_1 tends to infinity with $\eta \rightarrow 1$ and $x_2 \rightarrow 0$, whilst N/V for l_2 tends to the finite value of $6/(\pi d_2^3)$ with $\eta \rightarrow 1$ and $x_2 \rightarrow 1$.

It must be noted that reduced densities in excess of hard sphere close-packing $\eta=0.74$ are obtained. This is an artefact of the hard sphere equations which have a pole at a reduced density of 1.0 so that densities in the range 0.0 to 1.0 are calculated.

4.8.3 System With $a_{11}=0$, $a_{12}=a_{22}/4$ And $a_{22}>0$

It is interesting to see what happens to the point-sphere mixture's phase behaviour when the point-sphere attractive interaction is decreased from the arithmetic mean to a value of $a_{12}=a_{22}/4$.

$$a_{11} = 0, \quad a_{12} = a_{22}/4, \quad a_{22} > 0$$

By using the hard core expression described in Section 4.3 with the appropriate attractive interactions, the reduced equation of state is

$$p_r = \frac{\eta(1+\eta(3x_2-2)+\eta^2-\eta^3x_2)T_r}{\eta_{c,2}Z_{c,2}x_2(1-\eta)^3} - \frac{1+x_2}{2x_2} \frac{A_{c,2}\eta^2}{\eta_{c,2}Z_{c,2}}$$

4.8.3.1 The Critical Lines -

The critical lines are determined by solving the conditions for critical points (Section 4.6) for the mixture of points and hard cores with $a_{12}=a_{22}/4$. Fig. 4.17 shows the resulting pressure-temperature projection of the PTx surface. As in the case of the arithmetic mean, two critical lines are calculated representing both gas-liquid and liquid-liquid phase coexistence.

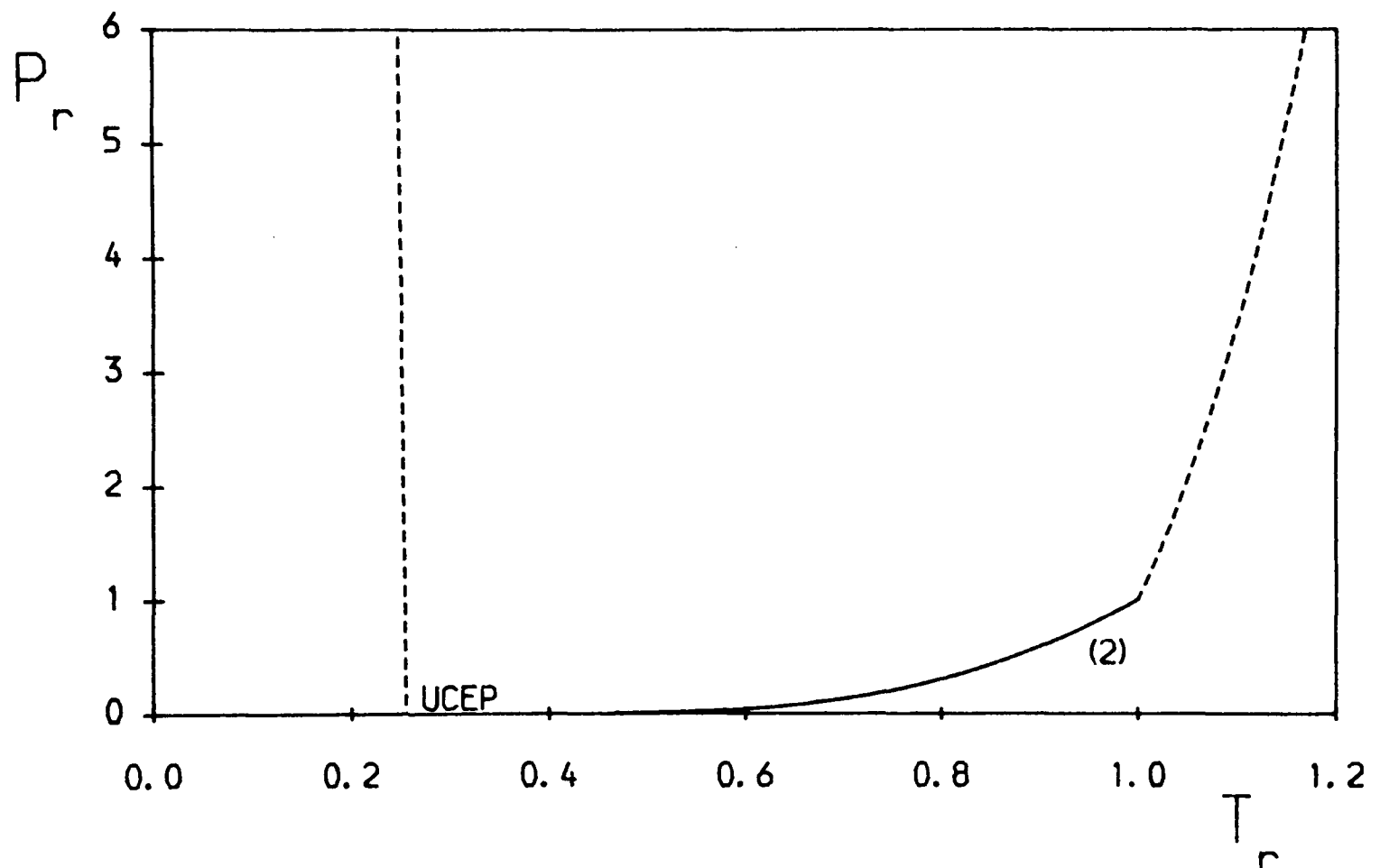
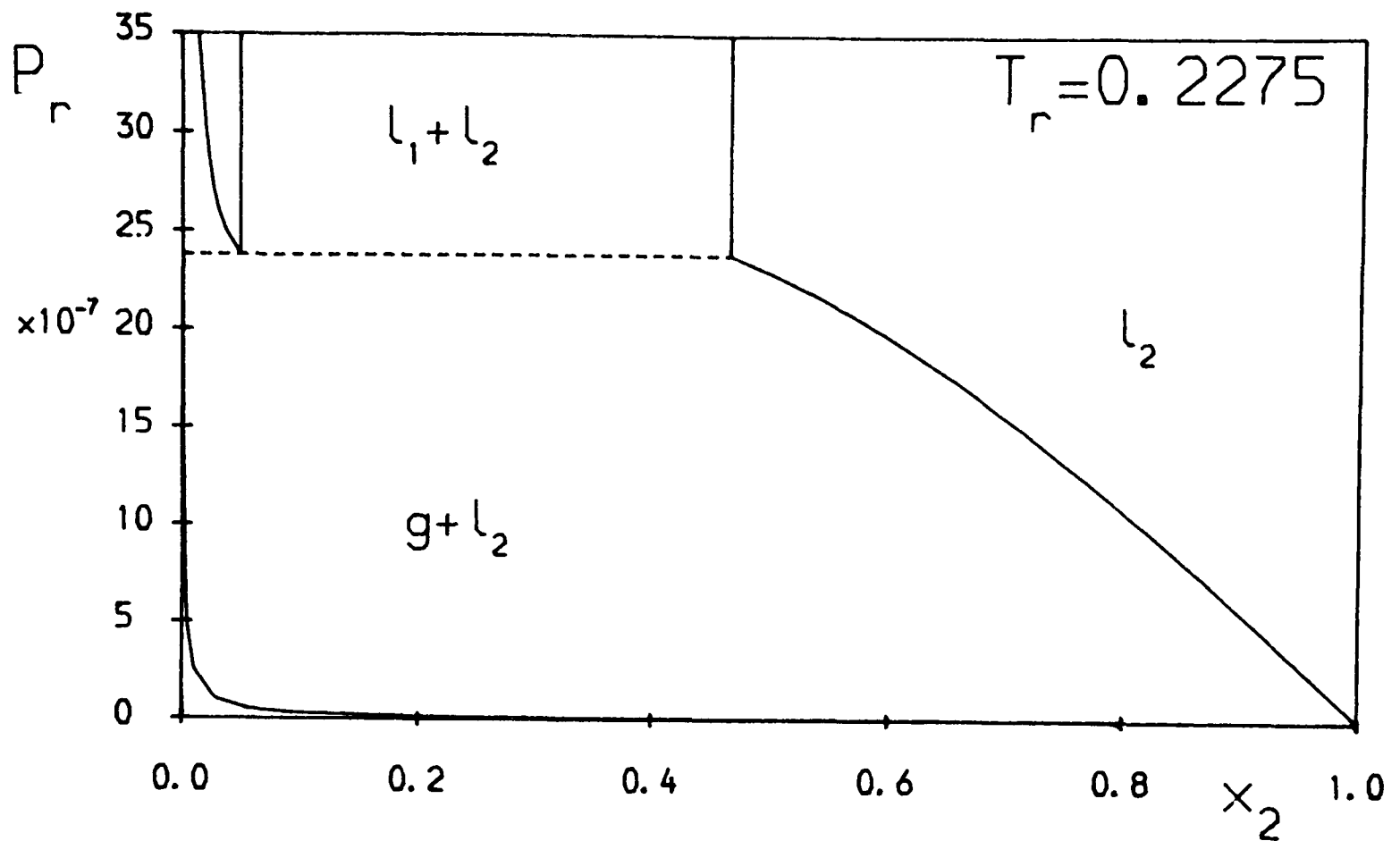


Fig. 4.17 The pressure-temperature projection for a binary mixture of point particles and hard cores with $a_{11}=0$ and $a_{12}=a_{22}/4$.

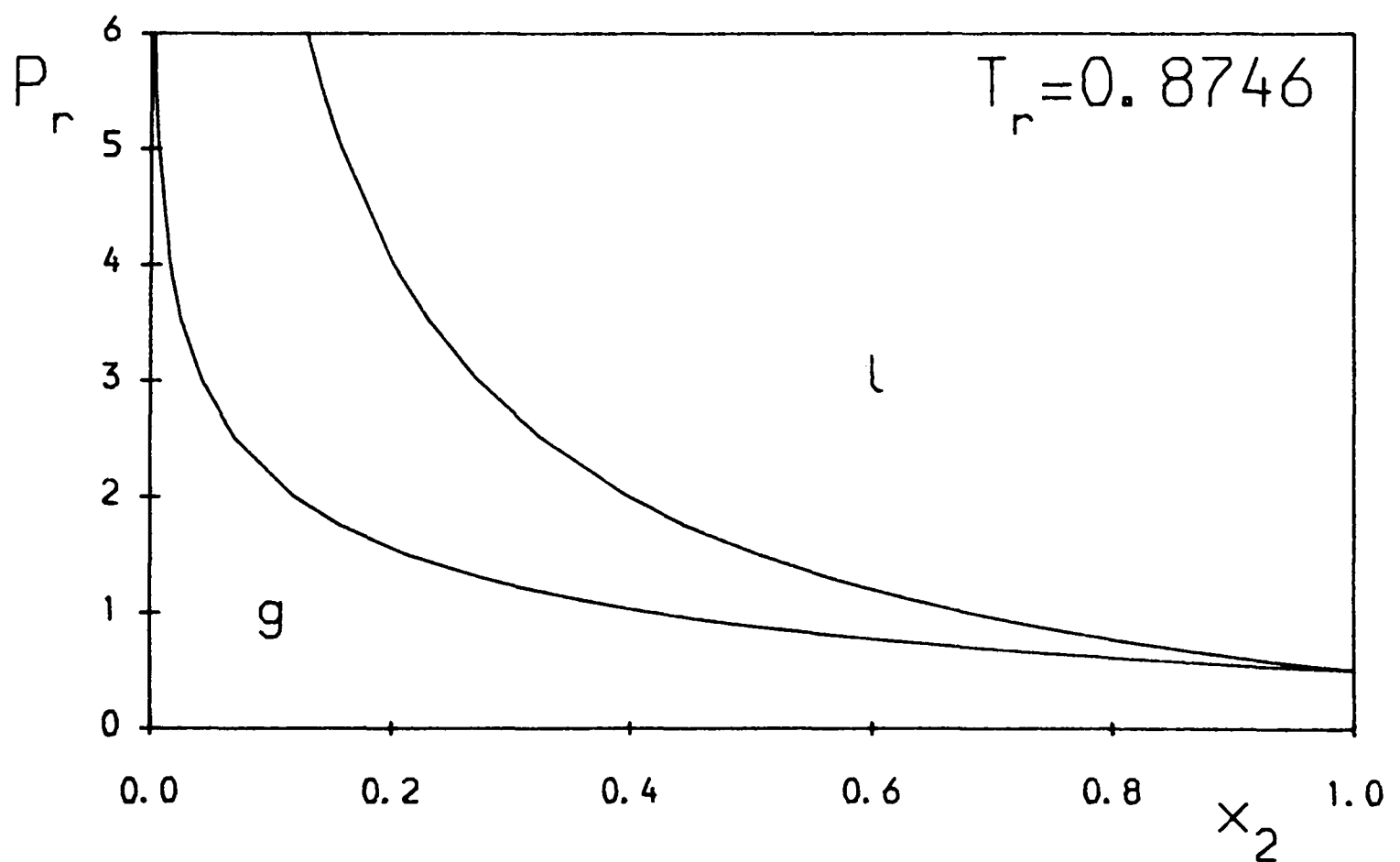
The gas-liquid critical line shows an increase in the reduced critical temperature and pressure with decreasing composition of spheres, corresponding to a positive slope for the line on the PT projection. Although the critical line occurs at lower critical temperatures than those calculated for the arithmetic mean $a_{12}=a_{22}/2$, "gas-gas immiscibility" is still the general feature of the critical behaviour (compare Fig. 4.15(a) with Fig. 4.17). As in the case of the arithmetic mean, the gas-liquid critical line has a limiting value of the critical temperature at infinite pressure corresponding to a reduced temperature of $T_r=2.6503=10.6012/4$.

The liquid-liquid critical line for the mixture of points and hard cores with $a_{12}=a_{22}/4$ is similar to the corresponding line found in the system with $a_{12}=a_{22}/2$. However, the extent of liquid-liquid coexistence has decreased considerably so that it is found only at much lower temperatures. The liquid-liquid critical line becomes metastable by intersecting a three phase line at a reduced UCEP temperature of $T_r=0.2553$ and pressure of $P_r=0.2182 \times 10^{-4}$. The corresponding liquid-liquid-gas three phase line lies just above the vapour pressure curve for the pure hard core system (2) due to the absence of azeotropy; it is not depicted on Fig. 4.17 because it occurs at very low pressures.

The nature of these critical lines will become clearer after an inspection of the isothermal pressure-composition phase diagrams described in the following section.

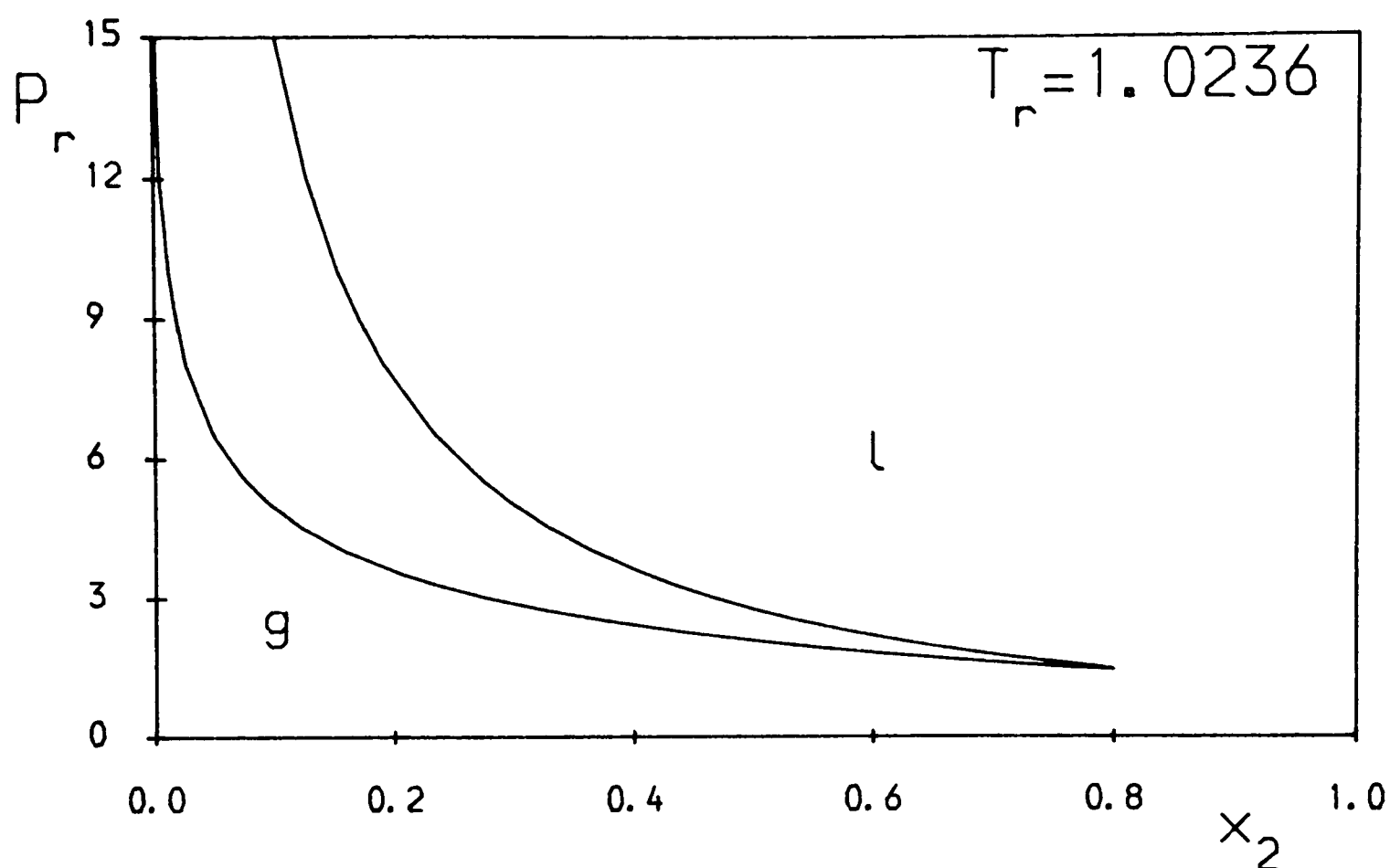


(a)



(b)

Fig. 4.18 Isothermal pressure-composition phase diagrams for a point-hard core mixture with $a_{11}=0$ and $a_{12}=a_{22}/4$.



(c)

Fig. 4.18(cont'd) Pressure-composition phase diagram for a point-hard core mixture with $a_{11}=0$ and $a_{12}=a_{22}/4$.

4.8.3.2 Pressure-Composition Phase Diagrams -

The pressure-composition phase diagrams calculated for the mixture of points and hard cores with $a_{11}=0$ and $a_{12}=a_{22}/4$ are shown on Fig. 4.18(a-c). At a reduced temperature of $T_r=0.2275$ which is below the UCEP temperature of $T_r=0.2553$, liquid-liquid as well as gas-liquid phase coexistence is seen (Fig. 4.18(a)). The corresponding liquid-liquid critical point occurs at high pressures and it is not shown on this diagram. The negative azeotrope found in the arithmetic mean system (see Fig. 4.14(a)) has disappeared so that liquid-liquid-gas three phase coexistence occurs at higher pressures than the vapour

pressure for the pure hard cores.

Fig. 4.18(b) represents a P_x phase diagram for a temperature above the UCEP; liquid-liquid immiscibility has disappeared leaving only gas-liquid coexistence. Gas-liquid critical points are found at temperatures above the critical point for the pure hard cores, and Fig. 4.18(c) shows the gas-liquid critical point corresponding to a temperature of $T_r=1.0236$.

4.8.3.3 The Temperature-Density Projection -

The extent of the liquid-liquid miscibility gap for the point-hard core mixture with $a_{12}=a_{22}/2$ is much greater than for the corresponding system with $a_{12}=a_{22}/4$. A comparison of the appropriate temperature-density projections showing liquid-liquid coexistence densities along the three phase line will clarify this point.

Fig. 4.19 clearly shows that the degree of liquid-liquid immiscibility is greater for the arithmetic mean curve (labelled 1/2) than for the $a_{12}=a_{22}/4$ curve (1/4) with UCEP temperatures of $T_r=0.7841$ and $T_r=0.2553$ respectively. There is also a substantial difference in the reduced UCEP densities with values of $\eta_2^1=0.5559$ for $a_{12}/a_{22}=1/2$ and $\eta_2^1=0.7226$ for $a_{12}/a_{22}=1/4$.

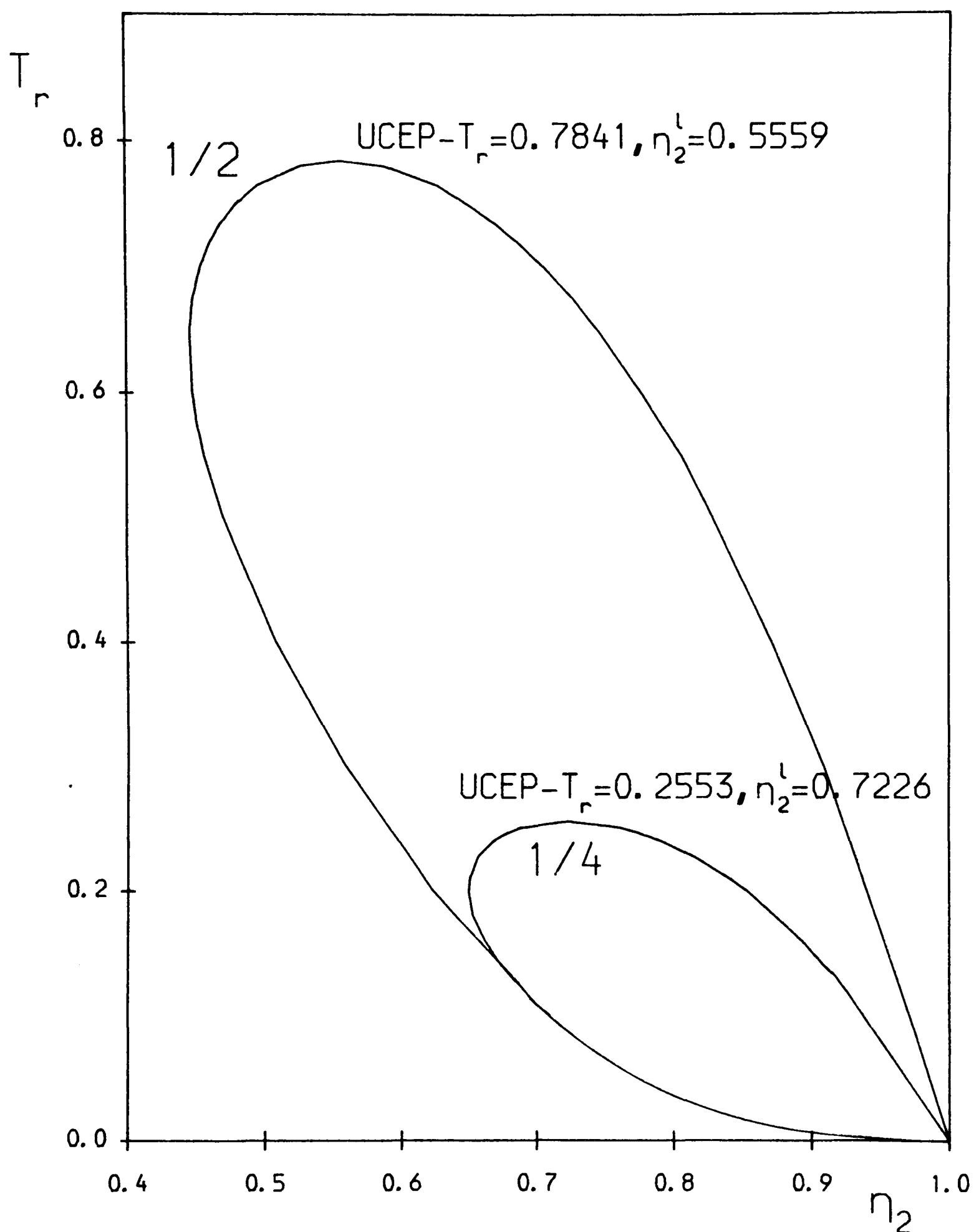


Fig. 4.19 Temperature-density projection showing the liquid densities along the three phase coexistence line for point-hard core mixtures with $a_{11}=0$ and with $a_{12}=a_{22}/2$ or $a_{12}=a_{22}/4$. Values of a_{12}/a_{22} are shown on the curves.

4.8.4 Varying The Point-Sphere Attractions.

This section presents a summary of the results obtained previously for binary mixtures of points and hard cores with $a_{11}=0$ and a_{12}/a_{22} values of 0, 1/4 and 1/2. Other systems with point-sphere attractions ranging between the geometric mean and the arithmetic mean are also investigated in order to determine the effect that varying the attractive interactions has on the phase behaviour of mixtures with infinite solute-to-solvent size ratio.

4.8.4.1 The Gas-Liquid Critical Lines -

The condition for critical points in mixtures (Section 4.6) are solved at various values of the point-sphere attractions to give the critical lines. The resulting gas-liquid critical lines are plotted on Fig. 4.20, and each curve is labelled with the appropriate value of a_{12}/a_{22} . A value of 0 corresponds to $a_{12}=0$ and a value of 0.5 represents $a_{12}=a_{22}/2$ etc.

The following trend emerges: as the point-sphere attractions are decreased (decreasing a_{12}/a_{22}), the gas-liquid critical lines move to lower critical temperatures with a corresponding decrease in the infinite-pressure temperature limit.

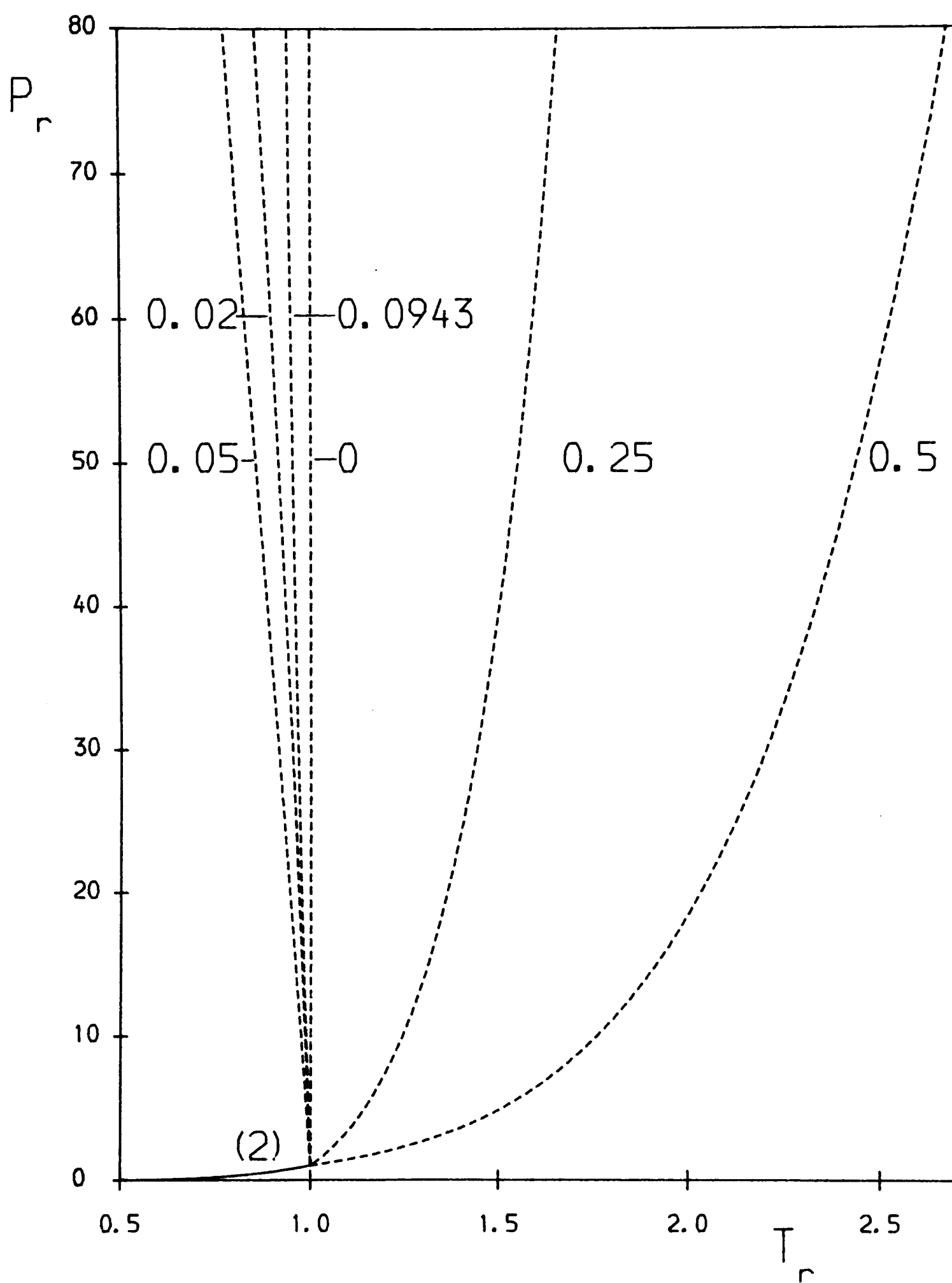


Fig. 4.20 Pressure-temperature projections of the gas-liquid critical lines for point-hard core mixtures with $a_{11}=0$. The various values of a_{12}/a_{22} are labelled on the curves.

"Gas-gas immiscibility of the first kind" is seen in the case of $a_{12}/a_{22}=0.5$ and to a lesser extent with the value of 0.25. This type of gas-liquid critical behaviour disappears at smaller values of the point-sphere attractive interactions. As a_{12} falls, the slope of the gas-liquid critical line steepens until it becomes vertical at about $a_{12}/a_{22}=0.1$; it is then negative (no gas-gas character) with a slope that passes through a minimum at about $a_{12}/a_{22}=0.05$, after which it rises until the critical line is identically vertical or isothermal at $a_{12}=0$.

4.8.4.2 The Liquid-Liquid Critical Lines -

Varying degrees of liquid-liquid immiscibility are found in the mixtures of points and hard cores investigated at different point-sphere attractions. The resulting critical lines are represented as PT projections in Fig. 4.21. The extent of liquid-liquid immiscibility is greatest at large values of a_{12} ; the UCEP temperature in the case of $a_{12}/a_{22}=0.5$ is $T_r=0.7841$ and for $a_{12}/a_{22}=0.25$ it is $T_r=0.2553$. Hence, the miscibility gap decreases with decreasing a_{12} until no liquid-liquid coexistence is found at $a_{12}=0$. The behaviour of the UCEP for various values of a_{12}/a_{22} is summarized below.

a_{11}	a_{12}/a_{22}	T_r^{UCEP}	P_r^{UCEP}
0	0.5	0.7841	0.1886
0	0.25	0.2553	2.2×10^{-4}
0	0.0943	0.0617	2.5×10^{-11}
0	0.0	0.0000	0.0000

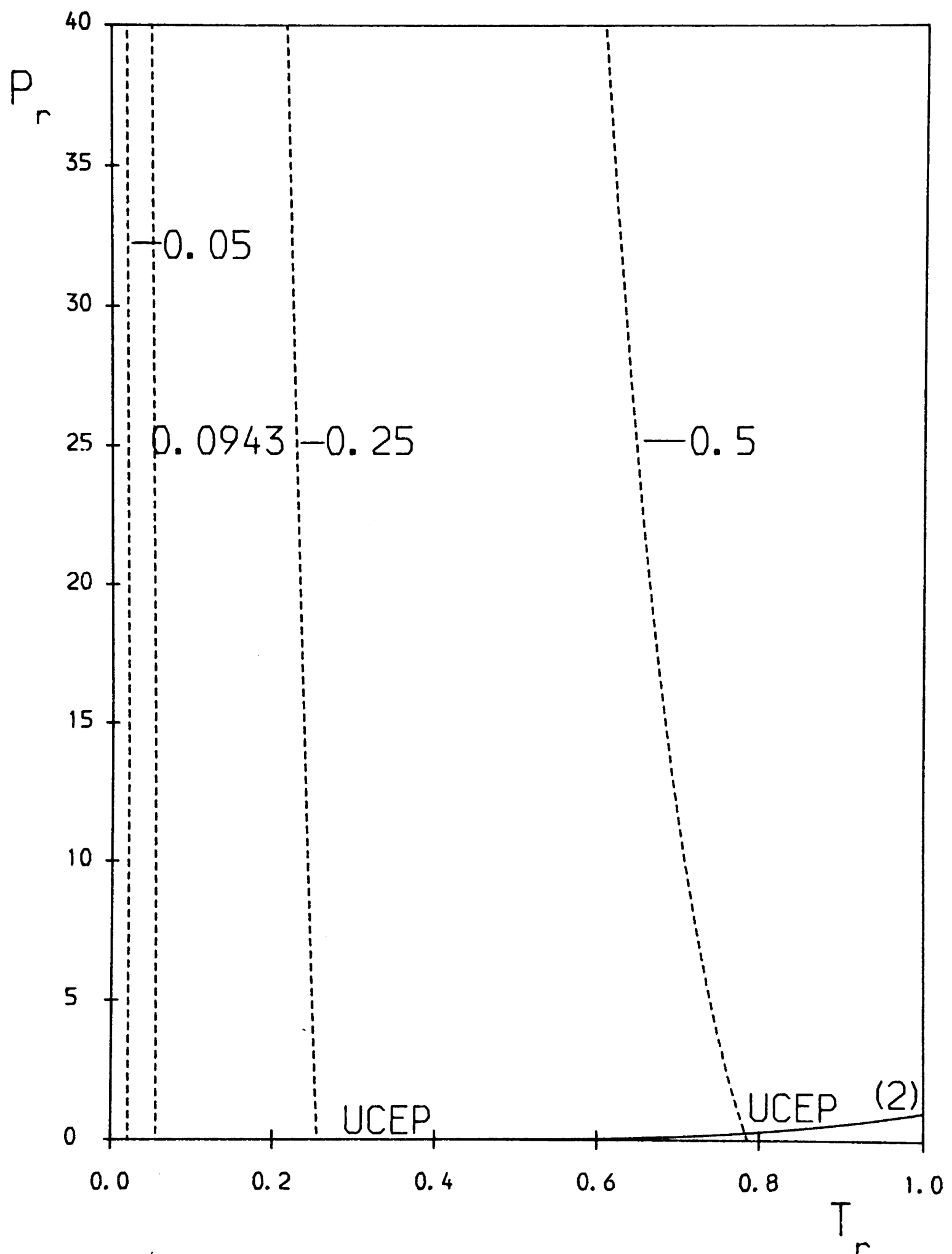


Fig. 4.21 PT projections of the liquid-liquid critical lines for point-hard core mixtures with $a_{11}=0$. The various values of a_{12}/a_{22} are labelled on the curves.

4.9 CONCLUSION

In this chapter the effect on the calculated phase diagrams of changing the point-sphere attractive interactions a_{12} for binary mixtures of point particles and hard core molecules is investigated. The simplest system comprises attracting spheres and point molecules without attractions among themselves or with the spheres, $a_{11}=0$ and $a_{12}=0$. This system has the same critical temperature and reduced density as the pure hard core system of Chapter 3 although the presence of the points increases the vapour pressure. When attractions are introduced between the point particles and the spheres $a_{12} \neq 0$, leaving $a_{11}=0$, the effective attractive interactions between the spheres are increased as the points interpose themselves freely between them. Such an effect lowers the vapour pressure of the mixture, and for values of a_{12} above about $a_{12}/a_{22}=0.1$ leads to "gas-gas immiscibility". The formation of a negative azeotrope at some value of a_{12} between $a_{12}/a_{22}=1/4$ and $a_{12}/a_{22}=1/2$ seems to be due to the same effect. More striking is that increasing a_{12} for the systems of points and hard cores leads to the equilibrium between two different liquid phases, one with a high mole fraction of points but a relatively high density of spheres, and the other with a low density of spheres but fewer points. The mechanism of phase separation involves a high proportion of the points interposing themselves between some of the larger spheres enhancing their attractive interactions to form a

dense phase, leaving behind a less dense phase richer in spheres. This effect leads to an increase in the extent of liquid-liquid immiscibility as the 1-2 forces are strengthened with the paradoxical rise of the upper critical end point, UCEP. The opposite trend is the more usual with systems of equal-sized spheres (Sections 5.1.5-5.1.11), where the transition from complete to limited liquid-liquid immiscibility occurs as a_{12} is lowered from above the arithmetic mean of a_{11} and a_{22} to below the mean.

We can conclude that by taking strong attractive interactions such as the arithmetic mean between the points and the hard cores, substantial liquid-liquid immiscibility is observed at moderate temperatures. Consequently, for the binary mixtures of hard core molecules with large size differences examined in the following chapter, the attractive interaction between the small (1) and large (2) spheres is taken as the arithmetic mean, $a_{12}=a_{22}/2$. As with the point-hard core mixtures described in this chapter there are no attractions between the small spheres, $a_{11}=0$.

A reasonable prediction is that the phase equilibria of hard core mixtures with large size differences will be qualitatively similar to the phase equilibria of point-hard core mixtures with the same attractions, and both systems become equivalent at an infinite size ratio.

CHAPTER 5

BINARY MIXTURES OF HARD CORES

The mixtures of points and hard cores (attracting spheres) of Chapter 4 showed regions of liquid-liquid immiscibility as well as the usual gas-liquid coexistence. In this chapter we examine the effect that the solute-to-solvent size ratio has on the phase equilibria of hard core mixtures with equivalent attractive interactions but different size ratios. The investigation will determine which particular features of the phase behaviour result from the existence of large size differences. The dependence of liquid-liquid coexistence on the hard core mixture's diameter ratio will be especially interesting. Mixtures of equal-sized hard cores are the first systems to be investigated with these arguments in mind.

5.1 MIXTURES OF EQUAL-SIZED HARD CORES $d_1=d_2$

Whilst mixtures of points and hard cores represent the limit of infinite diameter ratio ($d_1/d_2=0$), mixtures of equal-sized hard cores are at the other end of the spectrum with a limit of $d_1/d_2=1$.

5.1.1 The Equation Of State

Since the two components of the hard sphere mixture are of equal size, the mixture's equation of state follows directly from the Carnahan-Starling equation for pure hard spheres (see Chapter 3) with the mean-field attractive term for mixtures.

$$P = \xi \frac{(1+\xi+\xi^2-\xi^3)}{b(1-\xi)^3} RT - \frac{a\xi^2}{b^2}$$

$$d_1=d_2=d, \quad b=\pi Ld^3/6, \quad \xi=b/V_m$$

$$a=a_{11}x_1^2+2a_{12}x_1x_2+a_{22}x_2^2$$

The equation of state is reduced with respect to the critical constants of pure component 2:

$$P_r = \xi \frac{(1+\xi+\xi^2-\xi^3)}{\eta_{c,2}Z_{c,2}(1-\xi)^3} T_r - \frac{A_{c,2}\xi^2}{\eta_{c,2}Z_{c,2}} (x_1^2a_{11}/a_{22}+2x_1x_2a_{12}/a_{22}+x_2^2)$$

and as before

$$P_r = P/P_{c,2}, \quad T_r = T/T_{c,2}$$

$$\eta_{c,2}=0.130444, \quad A_{c,2}=10.6012, \quad Z_{c,2}=0.358956$$

5.1.2 The Free Energy And Chemical Potentials

By integrating the mixture's pressure with respect to volume, an expression for the Helmholtz free energy is obtained.

$$A_m = Lx_1\mu_1^0 + Lx_2\mu_2^0 + x_1RT \ln(x_1RT/V_m) + x_2RT \ln(x_2RT/V_m) - RT \frac{(3\xi^2 - 4\xi)}{(1-\xi)^2} - (a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2) \xi/b$$

The molar chemical potential for each component is determined from the free energy by differentiation.

$$\begin{aligned} \mu_1 &= L\mu_1^0 + RT \ln(x_1RT/V_m) + \frac{8\xi - 9\xi^2 + 3\xi^3}{(1-\xi)^3} RT \\ &\quad - 2(a_{11}x_1 + a_{12}x_2) \xi/b \\ \mu_2 &= L\mu_2^0 + RT \ln(x_2RT/V_m) + \frac{8\xi - 9\xi^2 + 3\xi^3}{(1-\xi)^3} RT \\ &\quad - 2(a_{12}x_1 + a_{22}x_2) \xi/b \end{aligned}$$

Mixed derivatives of the Helmholtz free energy with respect to volume and composition are used to determine the critical points for the mixtures of equal-sized hard cores, and the system's phase coexistence is examined using the expressions obtained for the chemical potentials. The techniques employed to determine the critical lines and phase equilibria for these mixtures with various attractive interactions are described in detail in Chapter 4 (Sections 4.6 and 4.7).

5.1.3 System With $a_{11}=0$, $a_{12}=0$ And $a_{22}>0$

In this case there are no attractive interactions between the molecules of species 1 ($a_{11}=0$), as well as no attractions between the molecules of species 1 and those of species 2 ($a_{12}=0$). Hence, the system is essentially a binary mixture of hard spheres and attracting spheres.

5.1.3.1 The Critical Line -

The gas-liquid critical line calculated for the equal-sized hard core mixture with these attractive interactions is shown as a pressure-temperature projection of the PTx surface in Fig. 5.1. An increase in the critical temperature with increasing pressure is observed indicating "gas-gas immiscibility of the first kind".

In contrast, the mixture of points and hard cores with the same attractive interactions (Section 4.8.1) showed no change in the critical temperature with composition. The critical temperature for the system of equal-sized spheres changes with composition because the spheres of component 1 exclude volume to the hard cores of component 2 (points do not). Hence, the intermolecular potential U_{12} is not zero everywhere and the system experiences a change in the critical temperature with composition.

Rigby et al. [53] have used perturbation theory to calculate the gas-liquid critical line for binary mixtures of hard spheres and square well molecules of equal core size, and their results are shown as squares on Fig. 5.1.

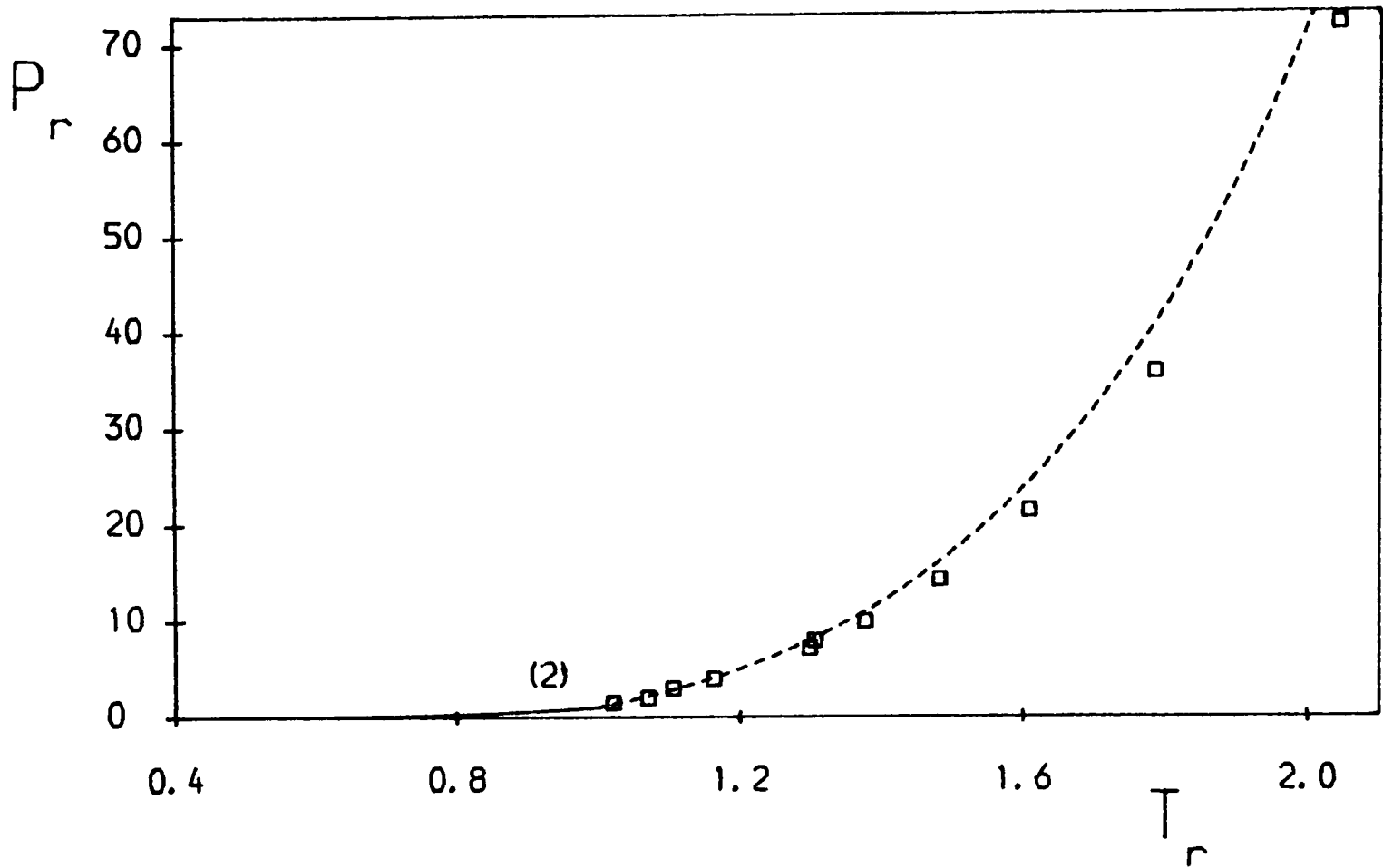


Fig. 5.1 PT projection for a mixture of equal-sized hard cores with $a_{11}=0$ and $a_{12}=0$. The squares are perturbation theory results for a mixture of spheres and square wells.

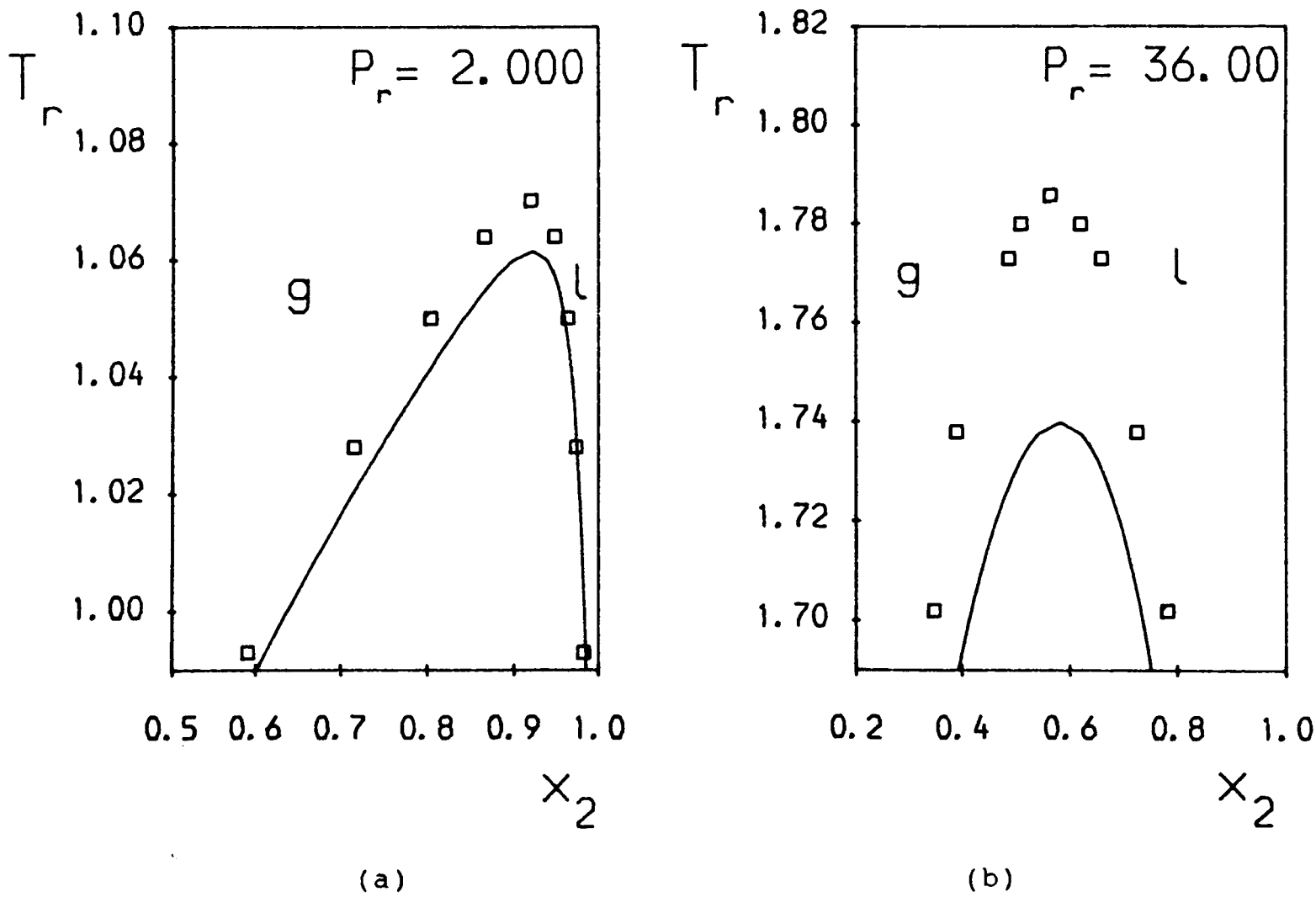


Fig. 5.2 Isobaric temperature-composition phase diagrams for equal-sized hard cores with $a_{11}=0$ and $a_{12}=0$. The squares represent the system of hard spheres and square wells.

It is clear that the mean-field results for the binary mixture of hard spheres and hard cores are in close agreement with the corresponding results for the equivalent mixture of hard spheres and square wells.

5.1.3.2 Temperature-Composition Phase Diagrams -

Fig. 5.2(a-b) shows the temperature-composition, T_x , phase diagrams for the system of equal-sized spheres with $a_{11}=0$ and $a_{12}=0$. Rigby et al. have also reported T_x phase diagrams for the mixture of spheres and square wells. Gas-liquid phase coexistence and critical points are seen at temperatures above the critical temperature for the pure square well system, confirming the "gas-gas immiscibility" predicted by the critical line. Good agreement between the mean-field and perturbation theories is seen even at high pressures.

5.1.4 System With $a_{11}=0$, $a_{12}=a_{22}/2$, And $a_{22}>0$

As with the point-hard core mixture of Section 4.8.2, which showed substantial liquid-liquid immiscibility, the attractive interactions between the spheres 1 and 2 are taken as the arithmetic mean, $a_{12}=a_{22}/2$. A comparison of the point-hard core results with the corresponding results for equal-sized spheres will be crucial in determining the effect that the solute-to-solvent size ratio has on the system's phase equilibria.

5.1.4.1 The Critical Line -

By solving the two conditions for critical points in binary mixtures using the appropriate derivatives of the free energy, critical points for a series of compositions are obtained. The gas-liquid critical line calculated for the mixture of equal-sized hard cores with $a_{11}=0$ and $a_{12}=a_{22}/2$ is plotted on Fig. 5.3 as a PT projection. The slope of the critical line is negative so that "gas-gas immiscibility" is not found, and it is also clear that there is no liquid-liquid critical line.

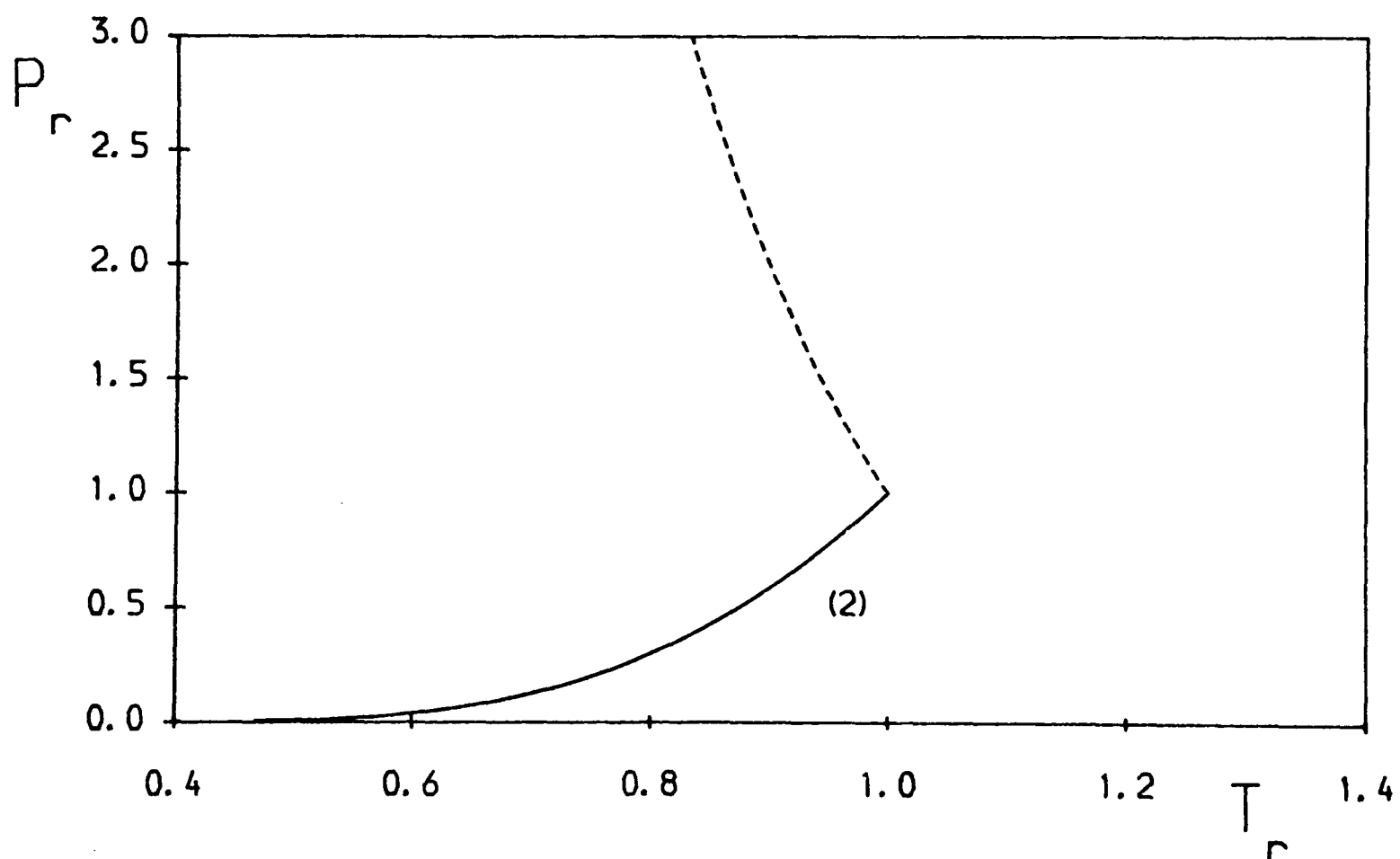
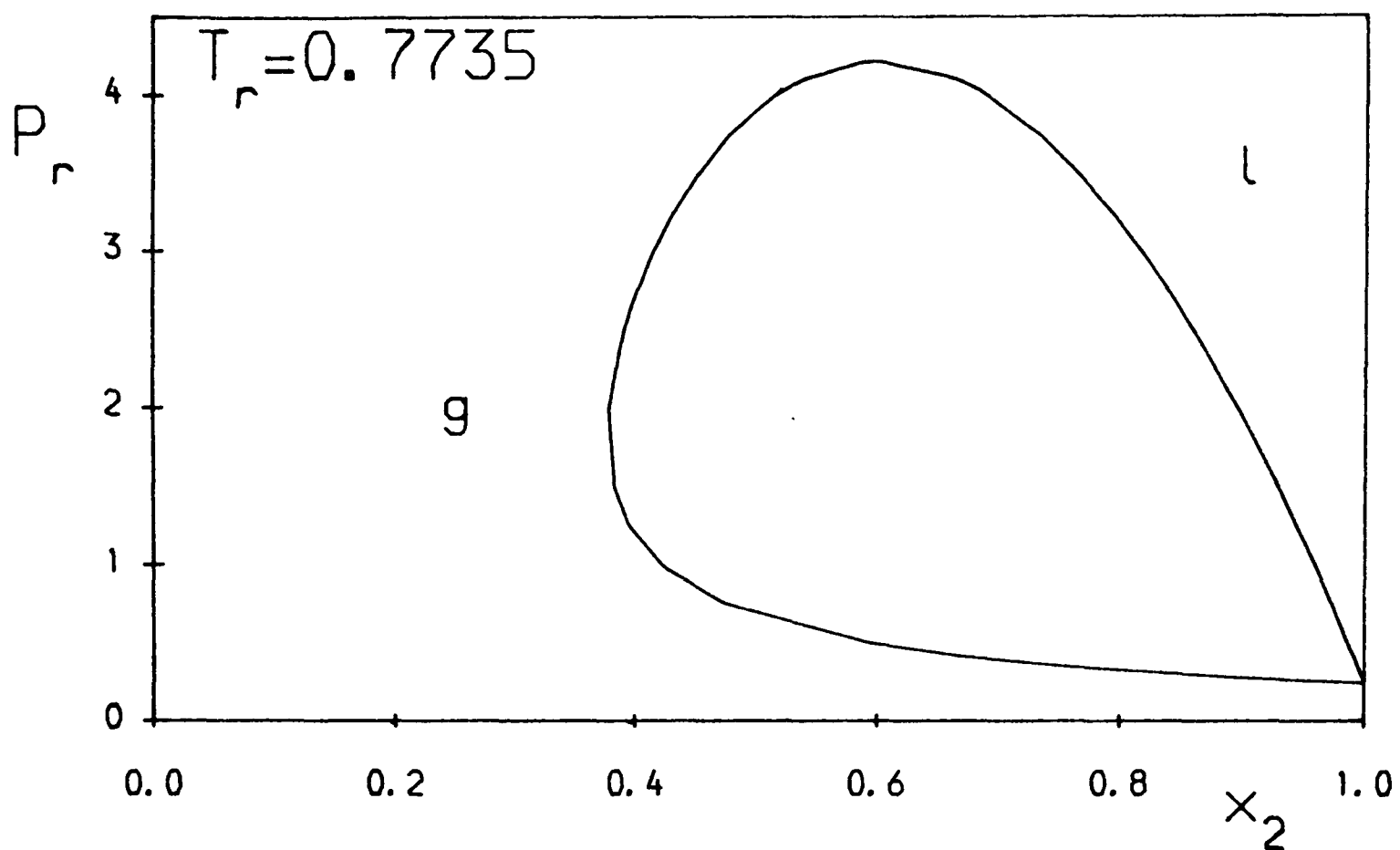


Fig. 5.3 The pressure-temperature projection for a binary mixture of equal-sized hard cores with $a_{11}=0$ and $a_{12}=a_{22}/2$.

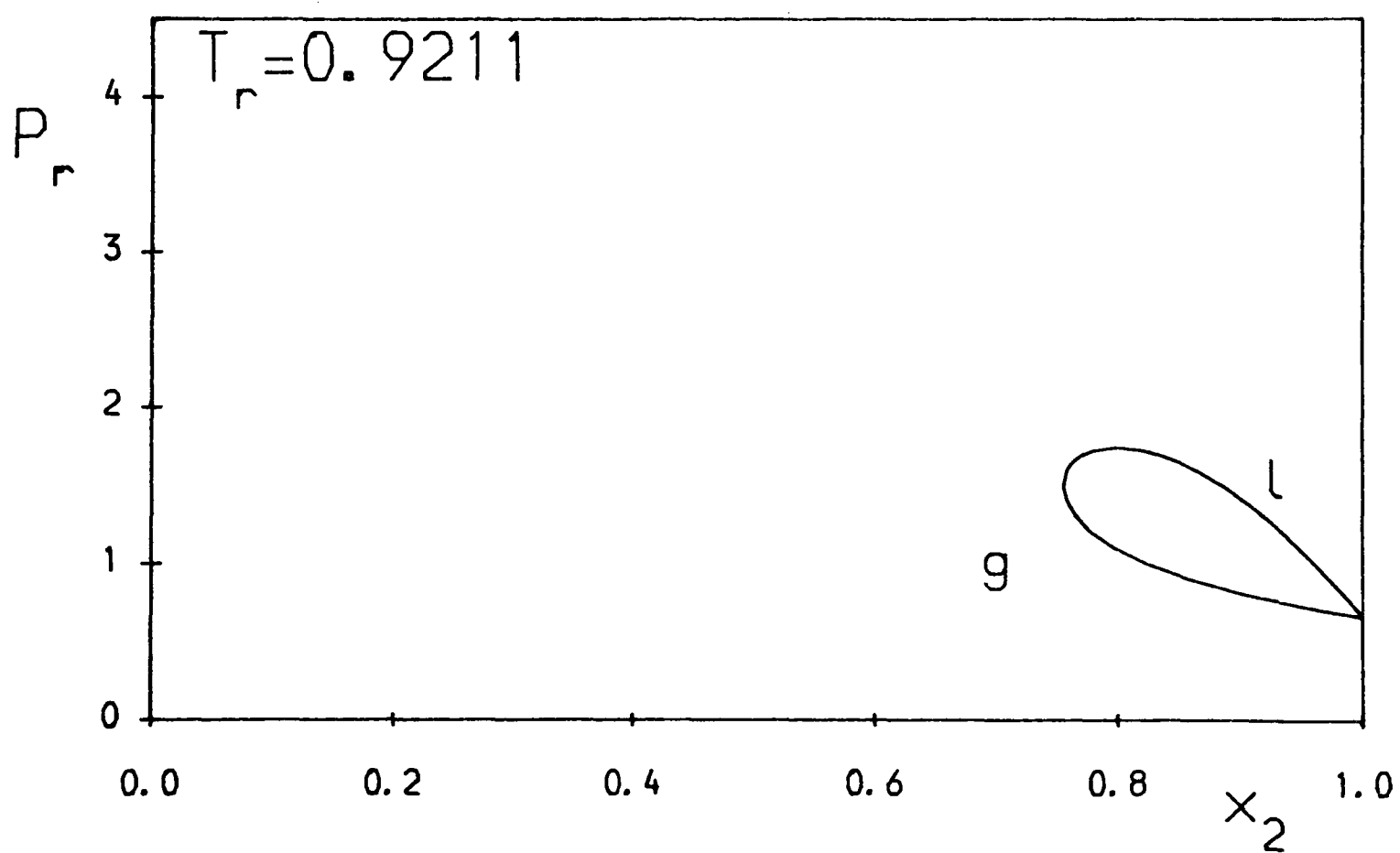
5.1.4.2 Pressure-Composition Phase Diagrams -

The isothermal pressure-composition phase diagrams calculated for the mixture of equal-sized hard cores are shown in Fig. 5.4(a-b). Gas-liquid coexistence is seen, and as predicted by the critical line, gas-liquid critical points are found at temperatures below the critical temperature for the pure hard cores (component 2). The gas-liquid critical pressure decreases as the temperature is increased; the reduced critical pressure of $P_r=4.2165$ at a temperature of $T_r=0.7735$ (Fig. 5.4(a)) decreases to a value of $P_r=1.7454$ at a temperature of $T_r=0.9211$ (Fig. 5.4(b)). At temperatures above the critical point of the pure hard cores there is no gas-liquid coexistence.

It is interesting to compare these phase diagrams with those obtained for the mixture of point particles and hard cores with the same attractive interactions, Fig. 4.14(a-e). In this system the gas-liquid critical points occur at temperatures above the pure system's critical point with "gas-gas immiscibility", whilst in the case of equal-sized spheres, the critical points occur at reduced temperatures below 1.0. However, the most interesting difference between the phase equilibria of these two systems is the absence of liquid-liquid coexistence. Liquid-liquid phase separation is not found in the phase diagrams of the mixture of equal-sized spheres whereas substantial liquid-liquid immiscibility appears in the mixture of points and hard cores under the UCEP temperature of $T_r=0.7841$.



(a)



(b)

Fig. 5.4 Pressure-composition phase diagrams for a mixture of equal-sized hard cores with $a_{11}=0$ and $a_{12}=a_{22}/2$.

Furthermore, the negative azeotrope found at low compositions with the mixture of points and hard cores is absent when the size ratio is one.

These arguments suggest that solvent-solute size differences play an important part in determining the type of phase behaviour that is observed. Although the extent of liquid-liquid immiscibility depends on the attractive interactions (see Section 4.8.4), large size differences are also important for liquid-liquid phase separation to be present in these systems. Thus liquid-liquid coexistence is found in the mixture of points and hard cores corresponding to maximal size difference, but not in the mixture of equal-sized hard cores.

However, it must be noted that liquid-liquid phase coexistence is possible for mixtures of equal-sized spheres with appropriate values of the attractive interactions. Van Konynenburg and Scott [5] report regions of liquid-liquid coexistence for mixtures of equal-sized van der Waals molecules with varying attractive interactions. The following sections examine the phase equilibria of mixtures of equal-sized hard cores with $a_{11}=a_{22}/2$ for different values of the ratio a_{12}/a_{22} , and the results are compared with those of van Konynenburg and Scott.

5.1.5 System With $a_{11}=a_{22}/2$, $a_{12}/a_{22}=0.8$, And $a_{22}>0$

Fig. 5.5 shows the pressure-temperature projections of the vapour pressure curves of components one (1) and two (2), and a gas-liquid critical line (dashed). As before the temperature and pressure are scaled with respect to the critical point of pure component 2. This simplest possible behaviour is referred to as Type I, with the loci of gas-liquid critical points joining the critical points of both pure components. Above a pressure of about $P_r=1.07$ there is no fluid-fluid equilibrium over the whole temperature range. No liquid-liquid immiscibility is seen with this system.

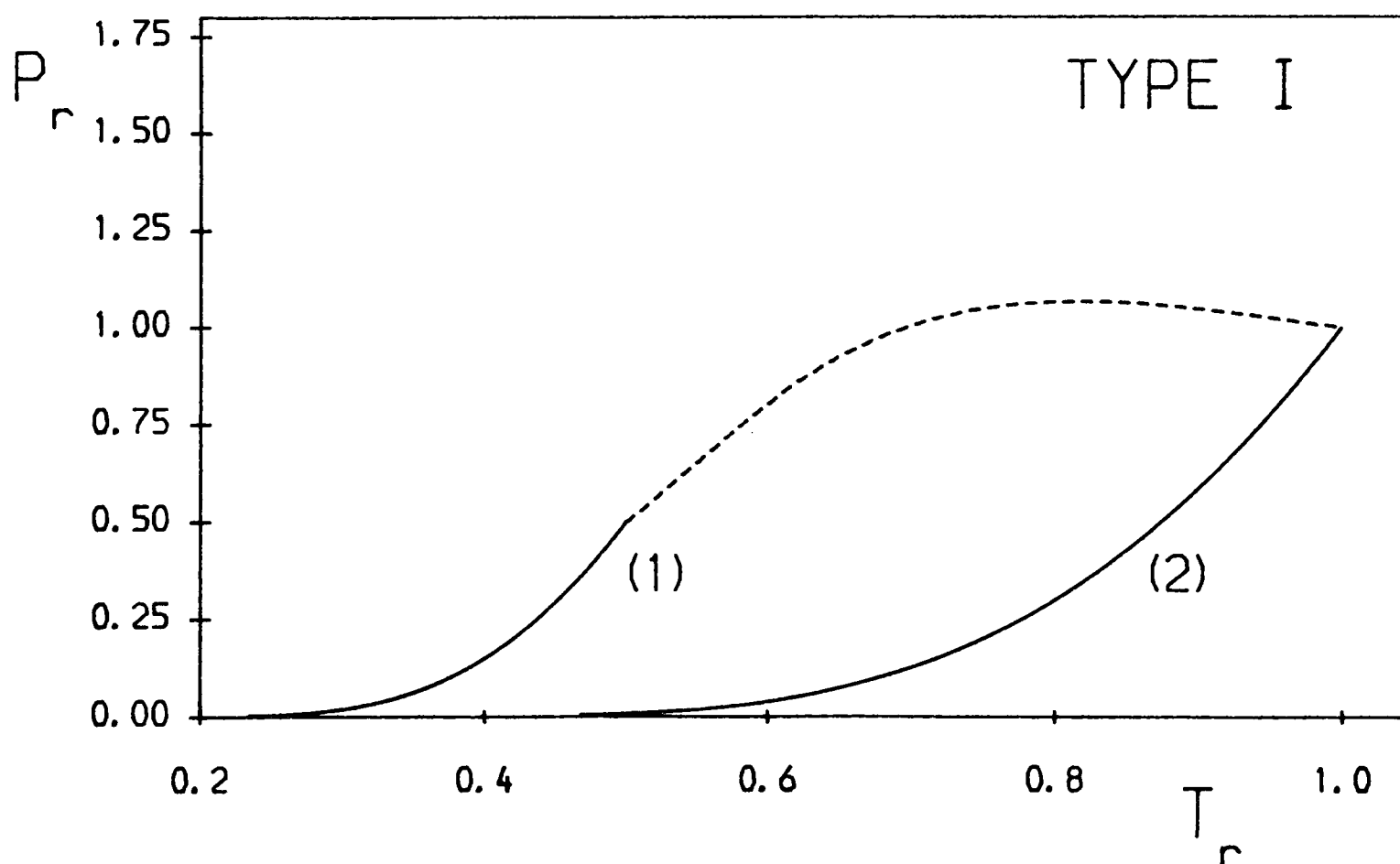


Fig. 5.5 The pressure-temperature projection for a binary mixture of equal-sized hard cores with $a_{11}=a_{22}/2$ and $a_{12}/a_{22}=0.8$.

5.1.6 System With $a_{11}=a_{22}/2$, $a_{12}/a_{22}=1/\sqrt{2}=0.7071$, And $a_{22}>0$

Liquid-liquid immiscibility appears in these systems when a_{12} is lowered below the arithmetic mean, $a_{12}/a_{22}=0.75$. The pressure-temperature projections of the critical lines for the mixture, with a_{12} taken as the geometric mean of a_{11} and a_{22} , $a_{12}/a_{22}=0.7071$, are depicted in Fig. 5.6. This system exhibits Type II phase behaviour. As with Type I systems, a gas-liquid critical line joins the critical points of the two pure components. There is also a liquid-liquid critical line ending at an upper critical end point UCEP when it meets a liquid-liquid-gas three phase line, l_1l_2g . The UCEP occurs at $T_r=0.4454$ and $P_r=0.2199$.

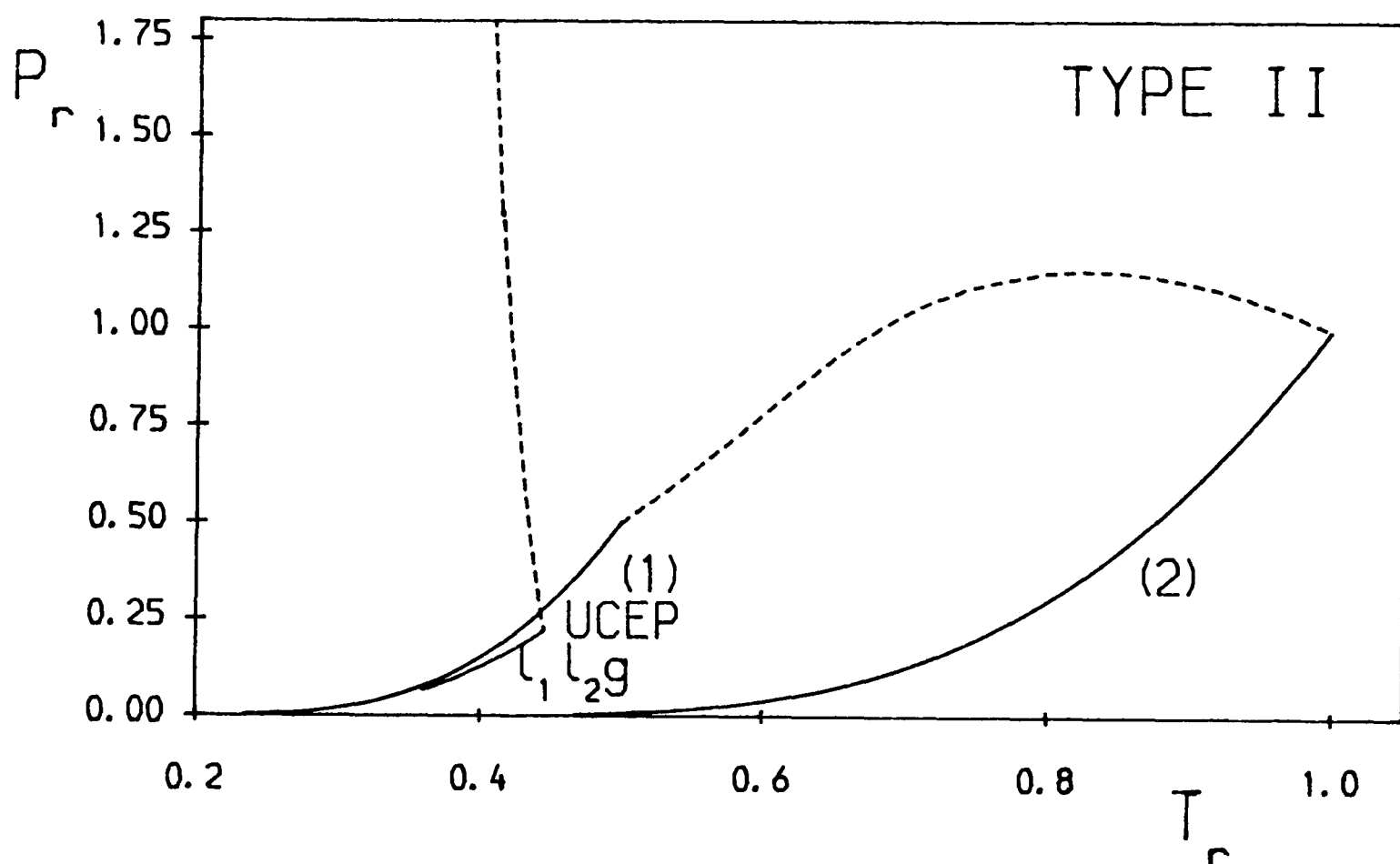


Fig. 5.6 The pressure-temperature projection for a binary mixture of equal-sized hard cores with $a_{11}=a_{22}/2$ and $a_{12}/a_{22}=0.7071$.

5.1.7 System With $a_{11}=a_{22}/2$, $a_{12}/a_{22}=0.69$, And $a_{22}>0$

The phase equilibria for a system with a value of a_{12} just below the geometric mean is summarized on a pressure-temperature projection in Fig. 5.7. As with the previous system, Type II behaviour is observed showing both gas-liquid and liquid-liquid coexistence. By decreasing the value of a_{12} , the extent of liquid-liquid immiscibility has increased. The upper critical end point for the mixture with $a_{12}/a_{22}=0.69$ occurs at a higher temperature and pressure ($T_r=0.5553$ and $P_r=0.5856$) than for the system with $a_{12}/a_{22}=0.7071$.

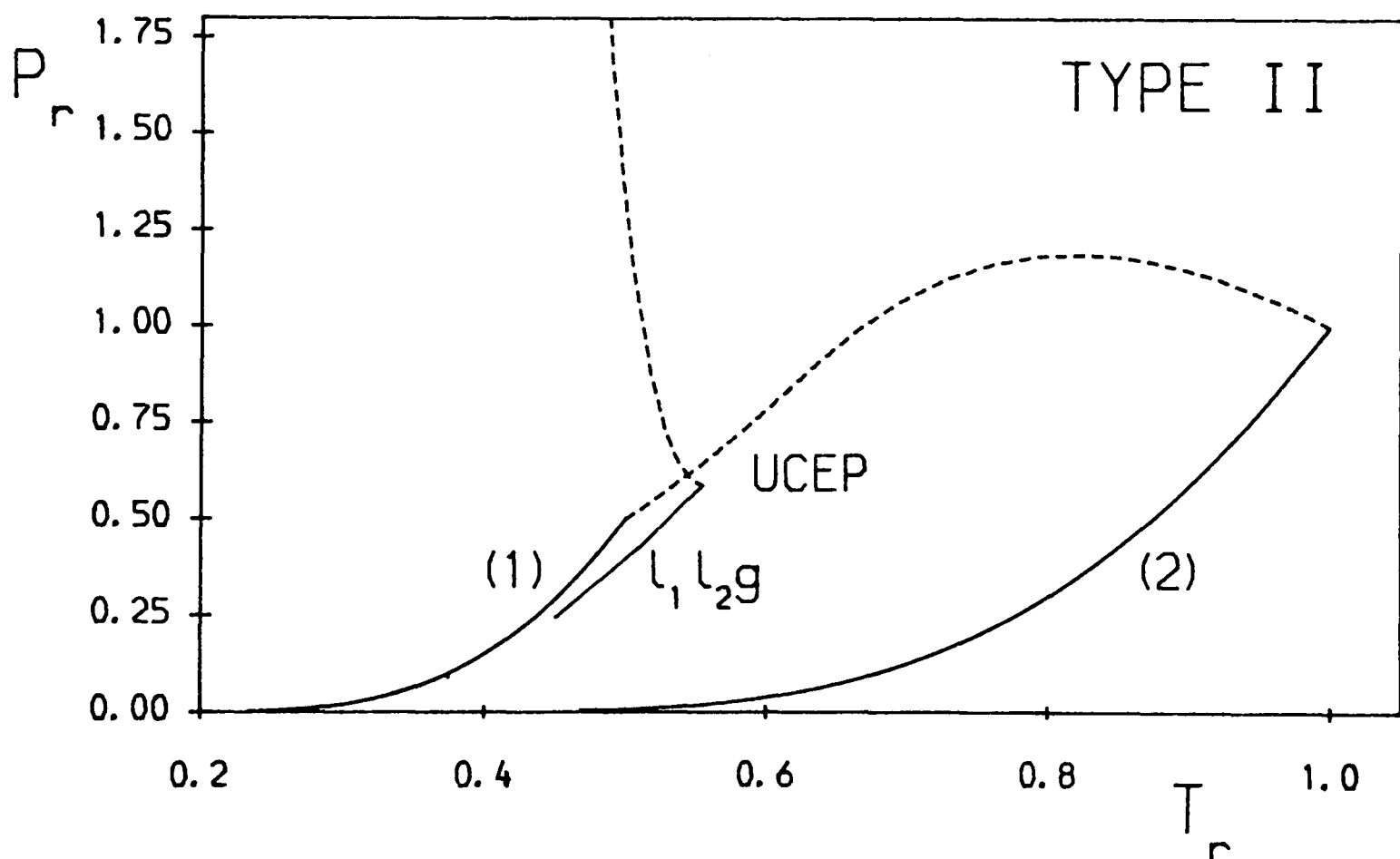


Fig. 5.7 The pressure-temperature projection for a binary mixture of equal-sized hard cores with $a_{11}=a_{22}/2$ and $a_{12}/a_{22}=0.69$.

5.1.8 System With $a_{11}=a_{22}/2$, $a_{12}/a_{22}=0.67$, And $a_{22}>0$

The extent of liquid-liquid immiscibility is increased even further as a_{12} is decreased to $a_{12}/a_{22}=0.67$. This system exhibits Type III phase behaviour as shown in Fig. 5.8. The locus of gas-liquid critical points, starting from the critical point of pure component 1, ends when it meets a three phase line at $T_r=0.5653$ and $P_r=0.6693$. The liquid-liquid critical line joins the gas liquid critical line which leaves from the critical point of pure component 2. These systems are sometimes denoted Type III_m because of the minimum seen in the critical line.

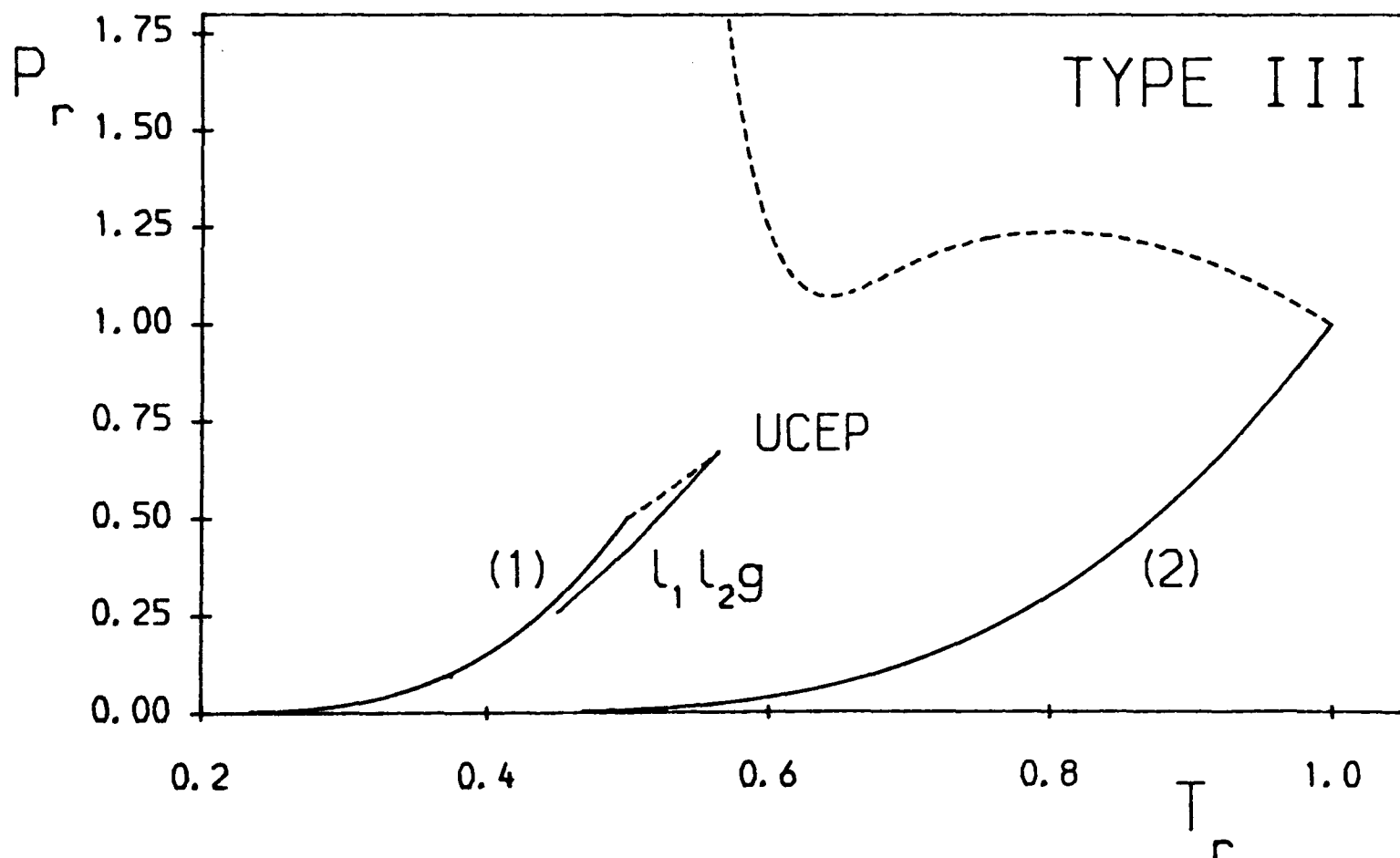


Fig. 5.8 The pressure-temperature projection for a binary mixture of equal-sized hard cores with $a_{11}=a_{22}/2$ and $a_{12}/a_{22}=0.67$.

5.1.9 System With $a_{11}=a_{22}/2$, $a_{12}/a_{22}=0.65$, And $a_{22}>0$

Fig. 5.9 depicts the pressure-temperature projections of the critical lines found for the system with $a_{12}/a_{22}=0.65$. This mixture also exhibits Type III phase behaviour with the appearance of two critical lines. The critical line representing the locus of the gas-liquid critical points starting from component 1 ends at an upper critical end point when the reduced temperature and pressure are $T_r=0.5389$ and $P_r=0.5924$. As before, the three phase coexistence line lies between the vapour pressure curves of the two pure components.

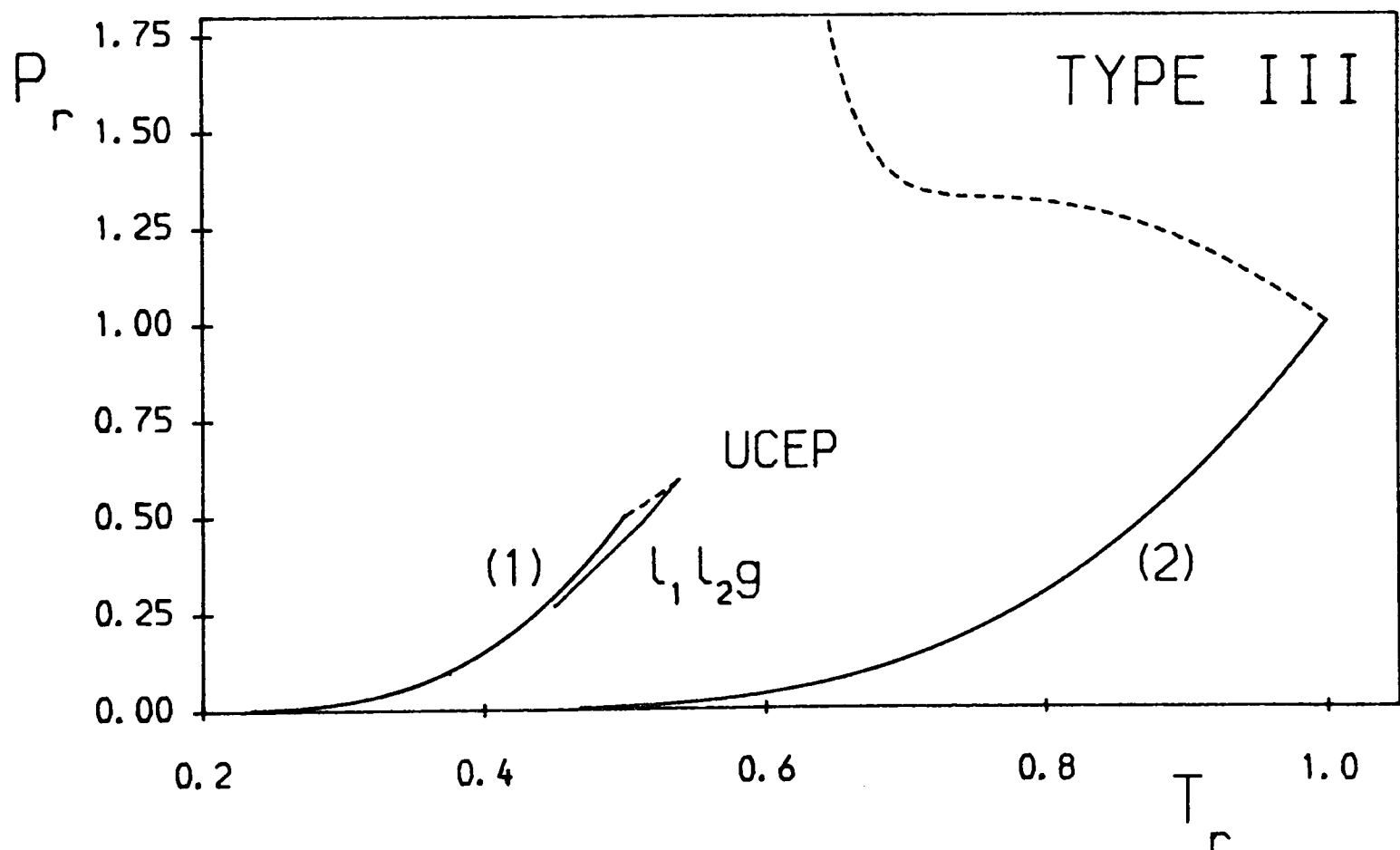


Fig. 5.9 The pressure-temperature projection for a binary mixture of equal-sized hard cores with $a_{11}=a_{22}/2$ and $a_{12}/a_{22}=0.65$.

5.1.10 System With $a_{11}=a_{22}/2$, $a_{12}/a_{22}=0.6$, And $a_{22}>0$

The final mixture of equal-sized hard cores investigated in this section is the system with $a_{11}=a_{22}/2$ and $a_{12}/a_{22}=0.6$. The pressure-temperature projections of the critical lines are represented in Fig. 5.10. Type III phase behaviour is found with an upper critical end point at $T_r=0.5136$ and $P_r=0.5274$. The slope of the critical line originating from the critical point of component 2 has become quite steep. In the next section the results obtained for the binary mixtures of equal-sized hard cores are summarized.

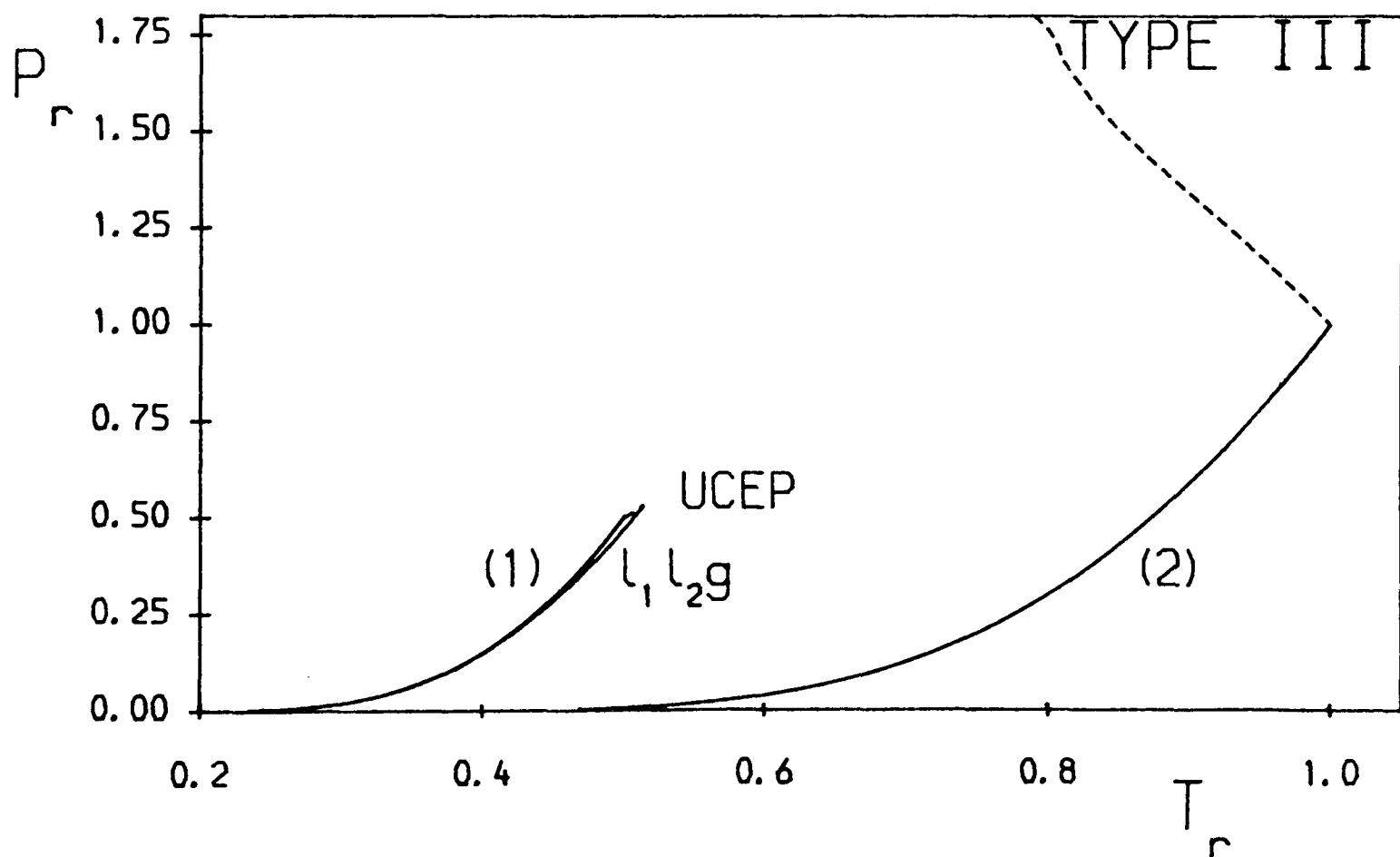


Fig. 5.10 The pressure-temperature projection for a binary mixture of equal-sized hard cores with $a_{11}=a_{22}/2$ and $a_{12}/a_{22}=0.6$.

5.1.11 Summary

A mixture of spheres of equal sizes, only one component of which has attractive forces (Section 5.1.3), shows strong "gas-gas immiscibility", as is found experimentally with mixtures containing helium [49].

The binary mixture of equal-sized hard cores with $a_{11}=0$ and $a_{12}=a_{22}/2$ (Section 5.1.4) has a much simpler phase behaviour than the equivalent system with $d_1/d_2=0$ (Section 4.8.2). The system of equal-sized spheres shows no region of liquid-liquid coexistence and no azeotrope.

Two component systems of equal-sized attracting spheres with $a_{11}=a_{22}/2$ were investigated in Sections 5.1.5-5.1.10 for different values of the ratio a_{12}/a_{22} , namely 0.8, $1/\sqrt{2}=0.7071$, 0.69, 0.67, 0.65, and 0.60. In the notation of van Konynenburg and Scott [5], the value of $a_{11}=a_{22}/2$ corresponds to $\eta=1/3$, and the values of a_{12}/a_{22} correspond to $\Delta=-0.0667$, 0.0572, 0.08, 0.1067, 0.1333 and 0.2 respectively. For their van der Waals fluids the first of these mixtures shows Type I behaviour, and the next five show Type II behaviour, and the transition from Type II to Type III occurs at $a_{11}=a_{22}/2$ and $a_{12}/a_{22}=0.58$. With the Mansoori equation of state the first system is again of Type I, the second and third are of Type II, but the last three are of Type III. The transition from Type II to Type III behaviour with $a_{11}=a_{22}/2$ is at about $a_{12}/a_{22}=0.68$, whilst the boundary between Types I and II remains at the arithmetic mean, $a_{12}/a_{22}=0.75$. Hence, the use of the

accurate hard sphere repulsive term reduces substantially the area occupied by Type II phase behaviour (liquid-liquid immiscibility) in the van Konynenburg and Scott η - Δ map.

In the next section we quantify the results obtained for the mixtures of point particles and hard cores (Chapter 4) by investigating the critical points and phase behaviour of binary mixtures of hard cores with large but finite size ratios.

5.2 BINARY MIXTURES OF HARD CORES $d_1 \neq d_2$

An equation of state for binary mixtures of hard cores of different sizes is available from the accurate representation for mixtures of hard spheres of Mansoori et al. (Chapter 1) with an appropriate mean-field attractive term (see Section 4.3).

$$P = \xi \frac{(1+\xi+\xi^2) - 3\xi(y_1+y_2\xi) - y_3\xi^3}{b(x_1r^3+x_2)(1-\xi)^3} RT - \frac{a\xi^2}{b^2(x_1r^3+x_2)^2}$$

with

$$r=d_1/d_2, \quad b=\pi L d_2^3/6, \quad \xi=b(x_1r^3+x_2)/V_m$$

$$y_1 = \frac{(d_1-d_2)^2(d_1+d_2)x_1x_2}{(d_1^3x_1+d_2^3x_2)}, \quad y_3 = \frac{(d_1^2x_1+d_2^2x_2)^3}{(d_1^3x_1+d_2^3x_2)^2}$$

$$y_2 = \frac{d_1d_2(d_1-d_2)^2(d_1^2x_1+d_2^2x_2)x_1x_2}{(d_1^3x_1+d_2^3x_2)^2}$$

$$a=a_{11}x_1^2+2a_{12}x_1x_2+a_{22}x_2^2$$

The equation is reduced with respect to the critical constants of pure component 2 (the larger sphere) to give

$$P_r = \xi \frac{(1+\xi+\xi^2) - 3\xi(y_1+y_2\xi) - y_3\xi^3}{\eta_{c,2}Z_{c,2}(x_1r^3+x_2)(1-\xi)^3} T_r - \frac{A_{c,2}\xi^2}{\eta_{c,2}Z_{c,2}(x_1r^3+x_2)^2} (x_1^2a_{11}/a_{22}+2x_1x_2a_{12}/a_{22}+x_2^2)$$

5.2.1 The Free Energy

By integrating the system's pressure with respect to volume, an expression for the molar Helmholtz free energy of the binary mixture of hard cores is obtained:

$$\begin{aligned}
 A_m = & Lx_1\mu_1^0 + Lx_2\mu_2^0 + x_1RT \ln(x_1RT/V_m) + x_2RT \ln(x_2RT/V_m) - RT \\
 & + RT[\xi(6-6y_1+2y_3) + 3\xi^2(-1+y_1-y_2-y_3)]/[2(1-\xi)^2] \\
 & - RT(1-y_3) \ln(1-\xi) - (a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2) \xi/[b(x_1r^3+x_2)]
 \end{aligned}$$

The free energy's derivatives with respect to composition and volume are then determined, and the two conditions for critical points are solved for the critical density at specific compositions. Although the procedure used to calculate the critical lines is identical to the one described in Section 4.6, the algebra was considerably more tedious than for the mixtures of points and hard cores. Consequently, the complicated expressions for the mixed derivatives of the free energy and the two conditions of criticality were checked using an algebraic manipulation program.

5.2.2 $d_1/d_2=1/20$, $a_{11}=0$, $a_{12}=a_{22}/2$, And $a_{22}>0$

The first system to be investigated is a mixture of hard cores with a diameter ratio of $d_1/d_2=1/20$ which is a reasonable measure of the solvent-to-solute size ratio in some micellar solutions. The attractive interactions between the smaller spheres are zero $a_{11}=0$, and the attractions between the small and large spheres are taken as the arithmetic mean $a_{12}=a_{22}/2$, enabling a comparison with the mixture of points and hard cores described in Section 4.8.2.

5.2.2.1 The Critical Lines -

The critical lines calculated for the hard core mixture with $a_{11}=0$ and $a_{12}=a_{22}/2$ are shown as pressure-temperature projections in Fig. 5.11. As for the mixture of points and hard cores with the same attractions, both gas-liquid and liquid-liquid critical lines are found.

The gas-liquid critical line shows "gas-gas immiscibility" and it is both qualitatively and quantitatively very similar to the line obtained for the point-hard core mixture (Fig. 4.15(a)). The liquid-liquid critical line ends at an UCEP when it meets the liquid-liquid-gas three phase line at a reduced temperature of $T_r=0.6571$ and a reduced pressure of $P_r=0.0567$. This UCEP temperature is lower than the corresponding value of $T_r=0.7841$ obtained for the point-hard core mixture (see Section 4.8.2.3), indicating that a size ratio of $d_1/d_2=1/20$

produces less liquid-liquid immiscibility than an infinite size ratio. It must be noted that the mixture's azeotropic line is not shown on the PT projection.

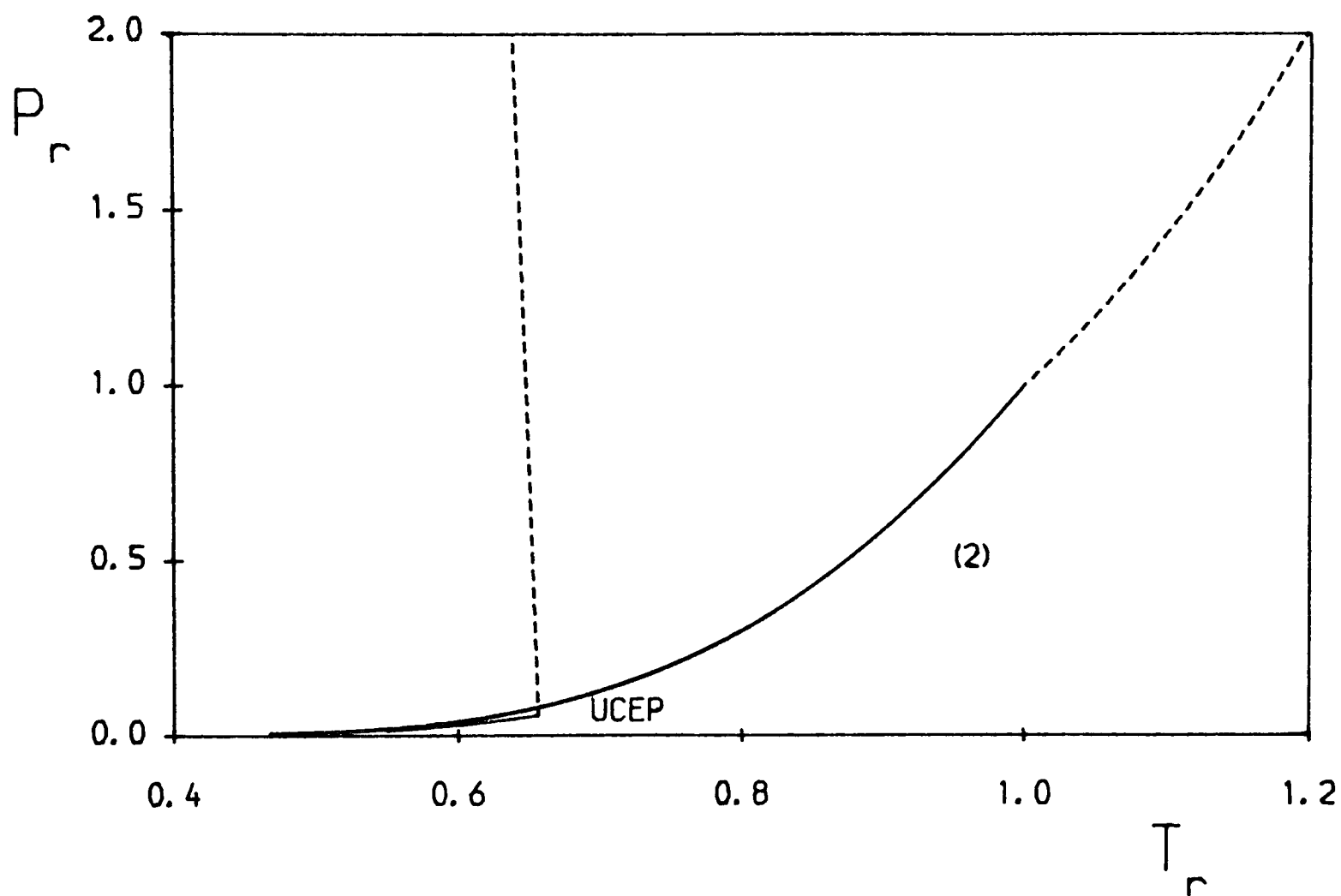
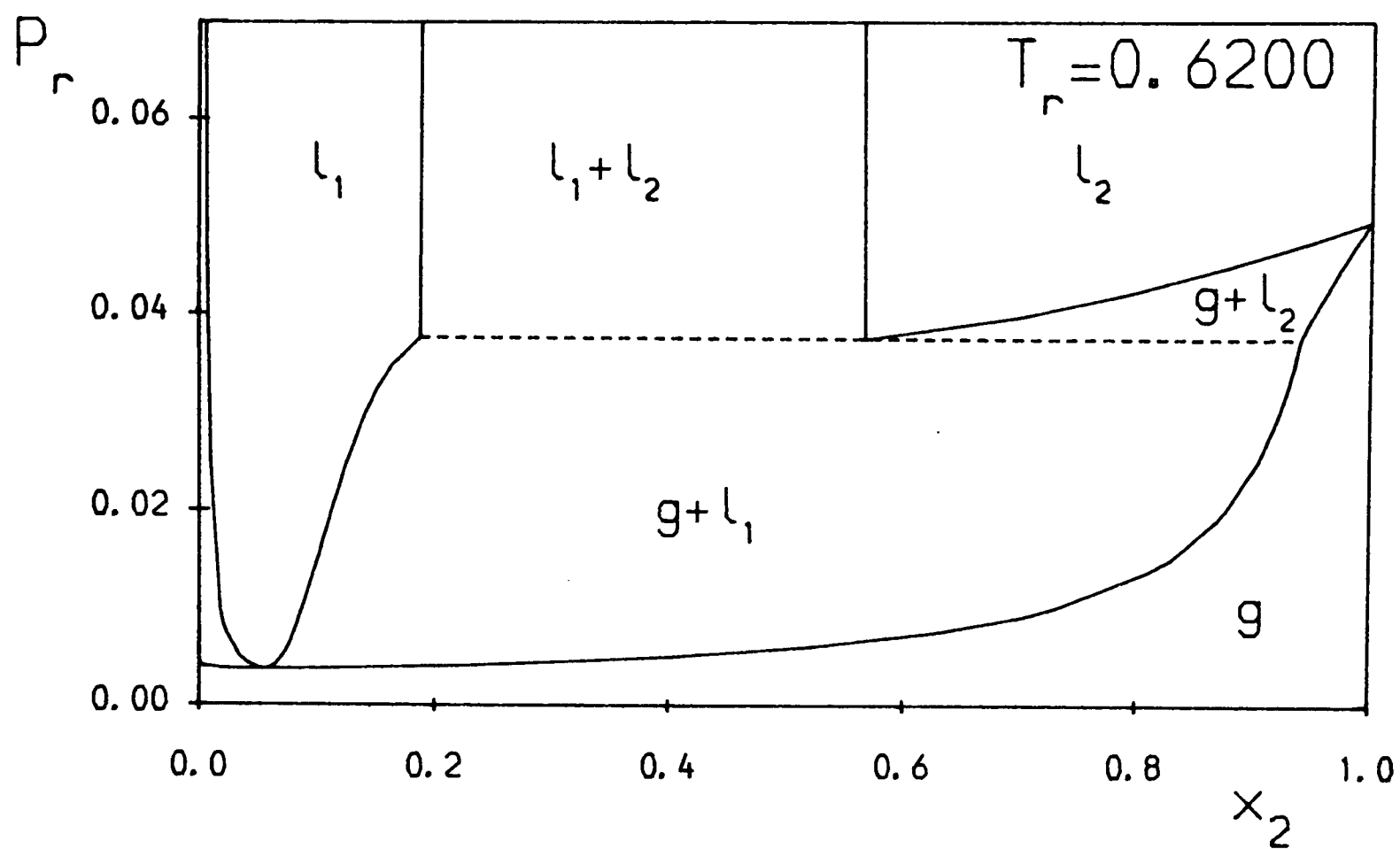


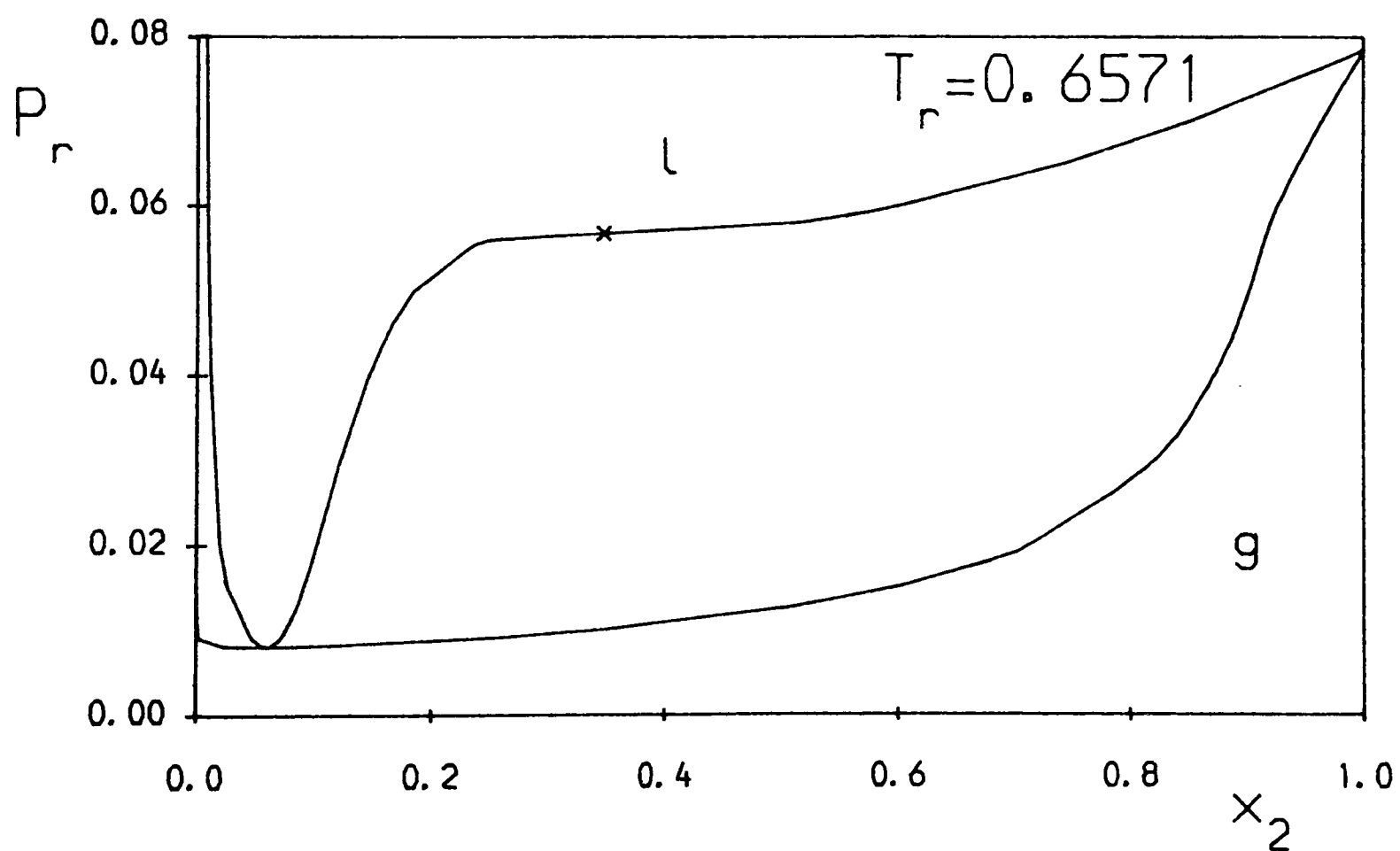
Fig. 5.11 The pressure-temperature projection for a binary mixture of hard cores with $d_1/d_2=1/20$, $a_{11}=0$ and $a_{12}=a_{22}/2$.

5.2.2.2 Pressure-Composition Phase Diagrams -

The Px phase diagrams for the mixture with $d_1/d_2=1/20$ are shown in Fig. 5.12(a-b) at constant temperatures of $T_r=0.6200$ and $T_r=0.6571$. Fig. 5.12(a) corresponds to a temperature of $T_r=0.6200$ below the UCEP so that both liquid-liquid and gas-liquid coexistence are found, and as with the point-hard core mixture, a negative azeotrope is seen.



(a)



(b)

Fig. 5.12 Pressure-composition phase diagrams for a mixture of hard cores with $d_1/d_2=1/20$, $a_{11}=0$ and $a_{12}=a_{22}/2$.

The P_x phase diagram at the UCEP temperature of $T_r=0.6571$ (Fig. 5.12(b)) indicates that the liquid-liquid coexistence has become thermodynamically metastable and only gas-liquid coexistence is found. The UCEP represents the flat portion of the coexistence curve and it is marked by an X on Fig. 5.12(b).

It is clear from these results that a greater degree of liquid-liquid immiscibility is obtained when the size difference between the small and large spheres is increased. The following calculations for mixtures with other diameter ratios will confirm this argument.

5.2.3 Varying The Size Ratio

The systems under investigation are binary mixtures of small (1) and large (2) hard core molecules with $a_{11}=0$ and $a_{12}=a_{22}/2$. Size effects are examined by varying the diameter ratio d_1/d_2 from the value of one, corresponding to hard cores of equal size, to the value of zero, corresponding to a mixture of points and hard cores. The critical lines and phase equilibria for the various diameter ratios are obtained in the normal way.

5.2.3.1 The Gas-Liquid Critical Lines -

Fig. 5.13 shows the PT projections of the gas-liquid critical lines calculated for the hard core mixtures with various size ratios, and the curves are labelled with the corresponding values of d_1/d_2 .

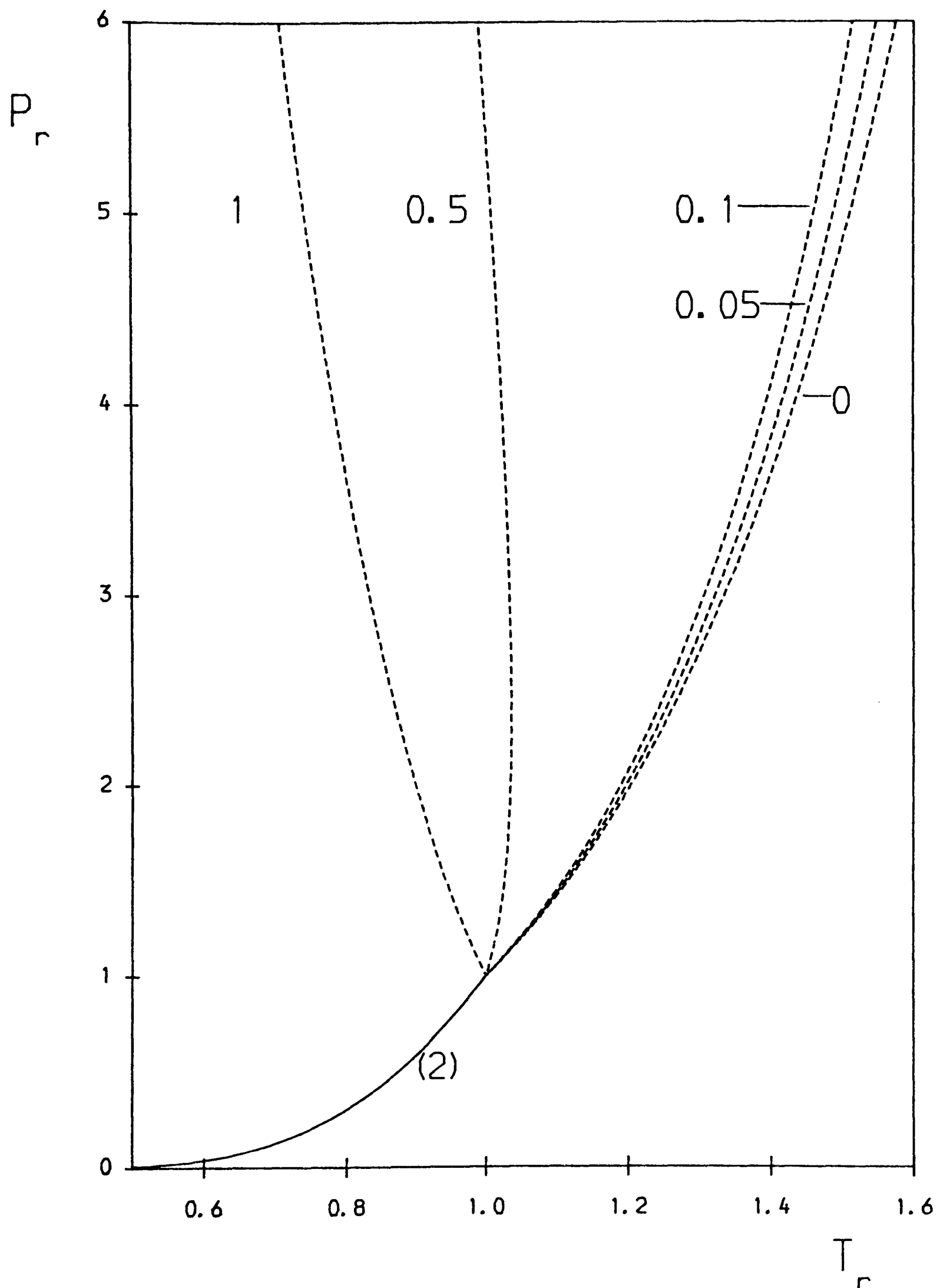


Fig. 5.13 Pressure-temperature projections of the gas-liquid critical lines for hard core mixtures with $a_{11}=0$ and $a_{12}=a_{22}/2$. The values of d_1/d_2 are labelled on the curves.

The critical lines obtained for $d_1/d_2=0.1$ and $d_1/d_2=0.05$ are very similar to the results calculated for the mixture of points and hard cores, labelled 0 on Fig. 5.13. On the other hand, an appreciable change in the slope of the gas-liquid critical line is seen when the spheres become similar in size; the line for $d_1/d_2=0.5$ is quite different from the lines obtained for large size ratios, and "gas-gas immiscibility" disappears altogether when the spheres are of equal size, $d_1/d_2=1$.

5.2.3.2 The Liquid-Liquid Critical Lines -

Liquid-liquid immiscibility is an important feature of the phase equilibria for binary mixtures with large size differences and with $a_{11}=0$ and $a_{12}=a_{22}/2$. The corresponding liquid-liquid critical lines are shown in Fig. 5.14.

The system with the greatest degree of liquid-liquid coexistence is the mixture of points and hard cores which has a value of $d_1/d_2=0$ and an UCEP temperature of $T_r=0.7841$. As the difference in size decreases, the area spanned by the liquid-liquid immiscibility is diminished; the upper critical solution temperature UCST for a mixture with $d_1/d_2=0.0333$ is $T_r=0.7030$, for $d_1/d_2=0.05$ it is $T_r=0.6571$ and for a diameter ratio of $d_1/d_2=0.0625$ the UCST has decreased to $T_r=0.6202$. The mixture of hard cores with a diameter ratio of $d_1/d_2=0.1$ shows limited liquid-liquid coexistence below reduced temperatures of about $T_r=0.5$, and the immiscibility finally disappears altogether with hard cores of equal size, $d_1/d_2=1$.

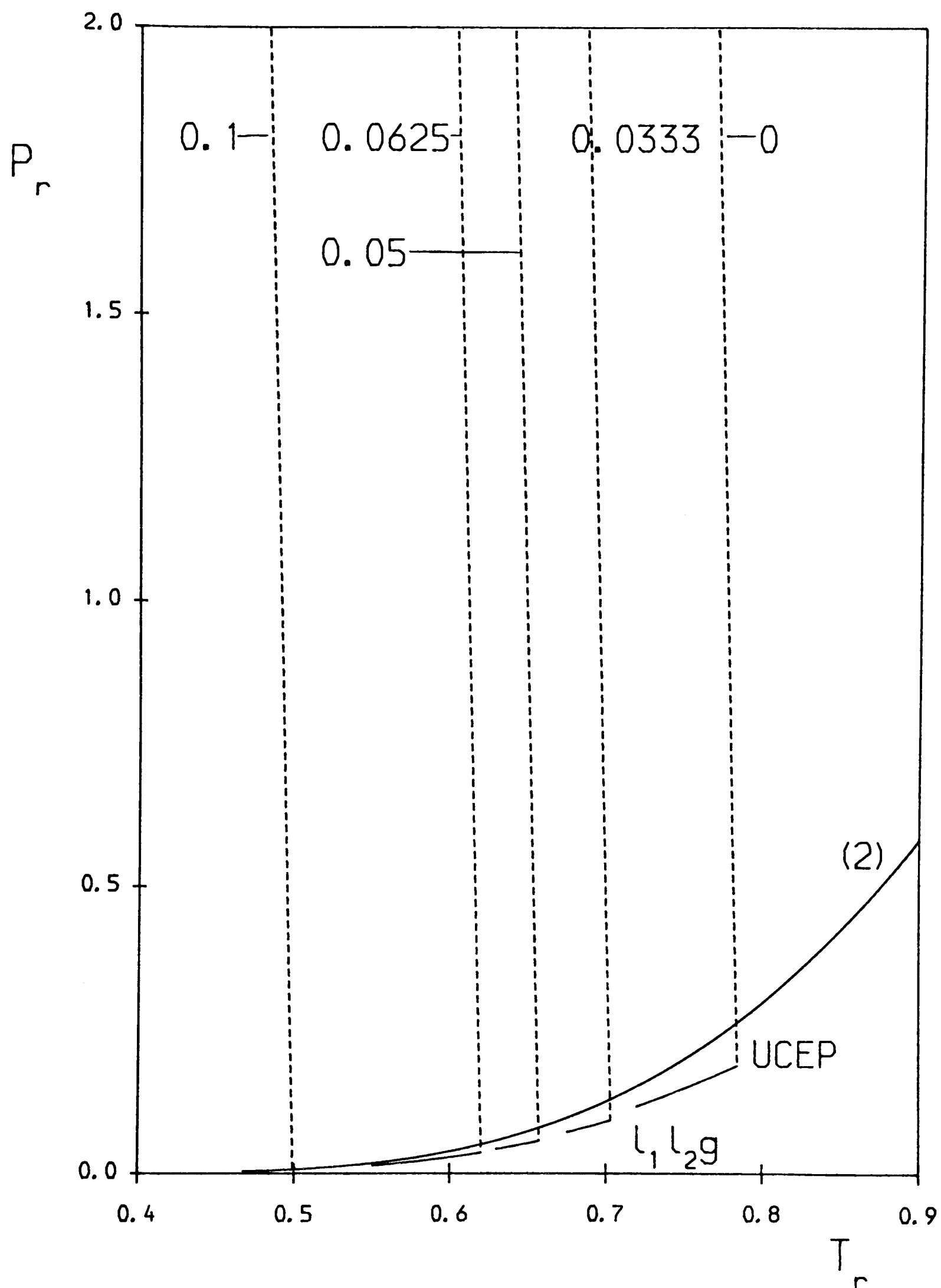


Fig. 5.14 PT projections of the liquid-liquid critical lines for hard core mixtures with $a_{11}=0$ and $a_{12}=a_{22}/2$. The values of d_1/d_2 are labelled on the curves.

5.2.3.3 Temperature-Density Projections -

It is now clear that the extent of liquid-liquid immiscibility depends quite dramatically on the magnitude of solute-solvent size differences. Fig. 5.15 represents the temperature-density projections of the liquid-liquid coexisting densities at three phase liquid-liquid-gas coexistence. As indicated in the previous section, the upper critical solution temperature decreases when d_1/d_2 increases so that the larger the size difference the greater the area of liquid-liquid immiscibility. It is worth noting that the hard sphere equation calculates unreasonably high values of the reduced density, which are in excess of the solidifying value of $\eta=0.5$.

The variation of the upper critical end point UCEP with diameter ratio d_1/d_2 is summarized in the following table:

d_1/d_2	T_r^{UCEP}	P_r^{UCEP}	η_2^l	η_2^g
0	0.7841	0.1886	0.5559	0.0109
1/30	0.7030	0.0924	0.5628	0.0059
1/20	0.6571	0.0567	0.5669	0.0039
1/16	0.6202	0.0362	0.5707	0.0026

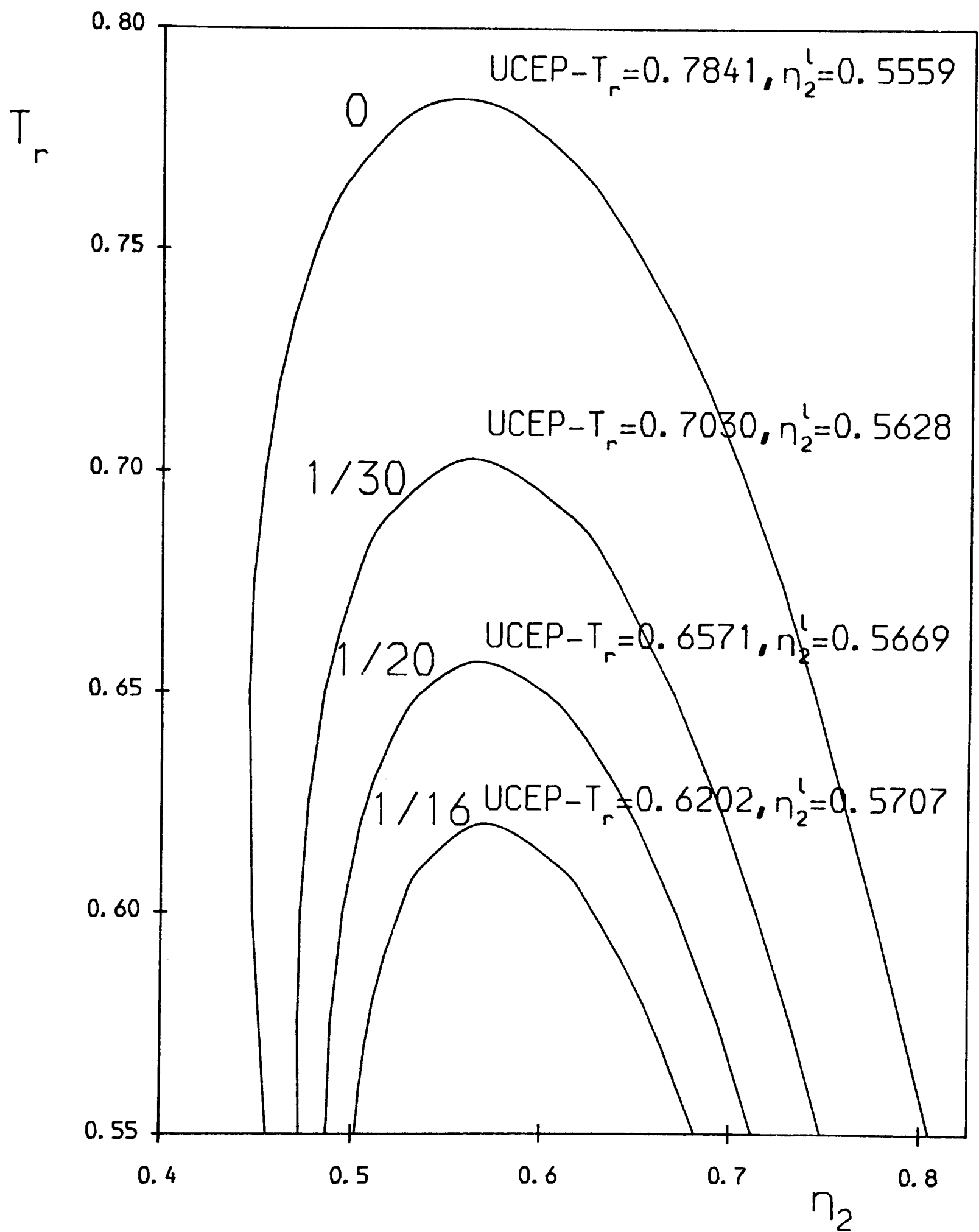


Fig. 5.15 Temperature-density projections of the coexisting liquid densities along the three phase line for hard core mixtures with $a_{11}=0$ and $a_{12}=a_{22}/2$. The values of d_1/d_2 are labelled on the curves.

The temperature-density projections for the hard core mixtures with the various diameter ratios can be compared by scaling the curves with the corresponding values of the UCEP temperature and reduced density. The solid line in Fig. 5.16 represents the mixture of points and hard cores, the triangles correspond to a size ratio of $d_1/d_2=1/30$, the squares to $d_1/d_2=1/20$, and the circles to $d_1/d_2=1/16$. The curves scale reasonably well indicating that similar mechanisms of phase separation are involved.

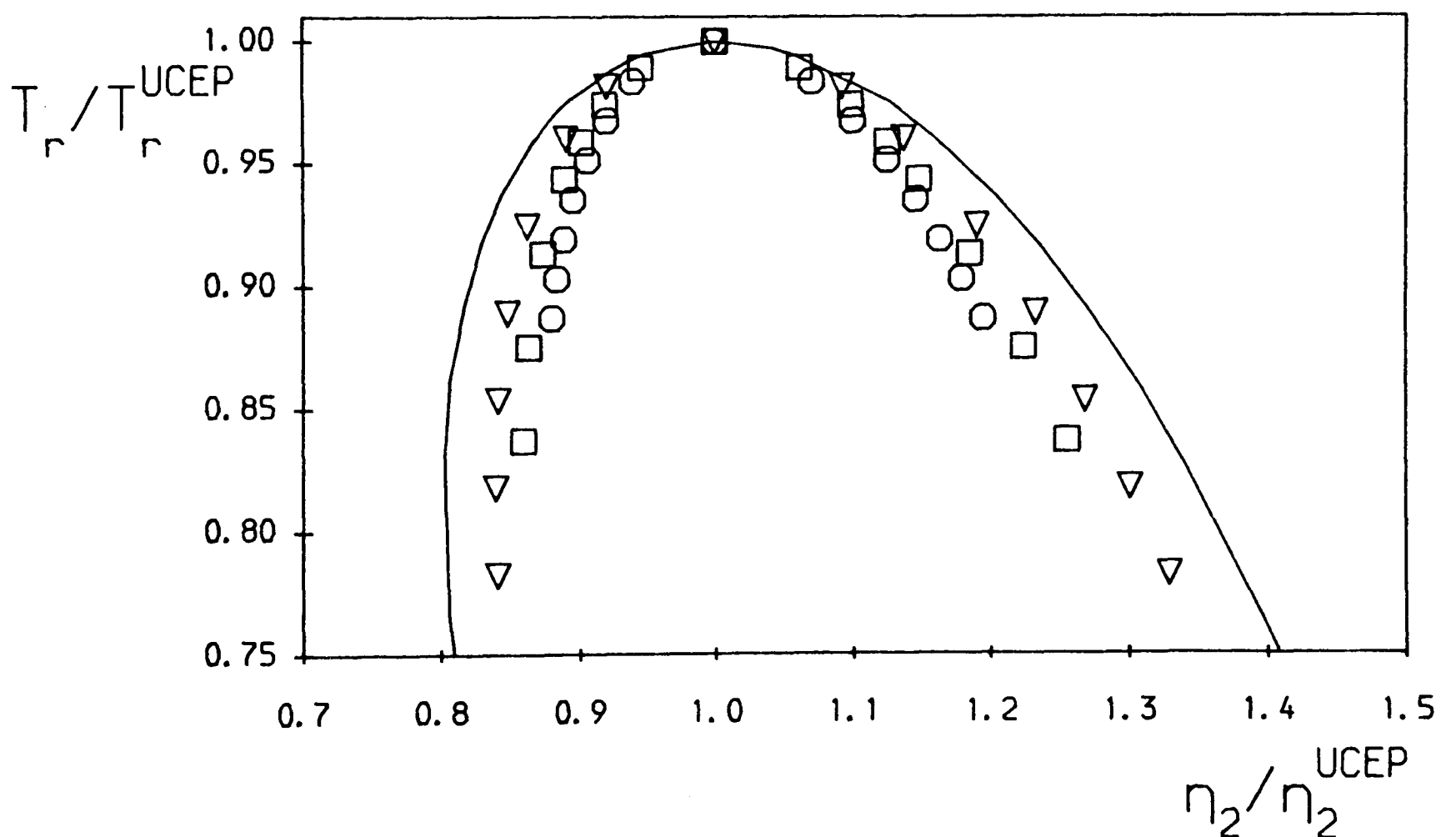


Fig. 5.16 Scaled temperature-density projections of the coexisting liquid densities for hard core mixtures with $a_{11}=0$ and $a_{12}=a_{22}/2$. Solid Curve, $d_1/d_2=0$; triangles, $d_1/d_2=1/30$; squares, $d_1/d_2=1/20$; circles, $d_1/d_2=1/16$.

5.3 CONCLUSION

In this final section the results obtained in Chapters 4 and 5 are summarized with special emphasis placed on the liquid-liquid coexistence. Two features were important in determining the extent of the liquid-liquid immiscibility found in the systems examined. The first involves the strength of the attractive interactions and the second involves the solvent-to-solute size ratio.

Calculations investigating the effect of varying the attractions between the small and the large spheres were performed in Chapter 4 for mixtures of points (1) and hard cores (2) with $a_{11}=0$ and with values of a_{12} ranging from zero to the arithmetic mean. Appreciable liquid-liquid immiscibility is found only at large values of the point-sphere attractive interactions such as $a_{12}=a_{22}/2$, and no liquid-liquid coexistence is found at $a_{12}=0$. Hence, the extent of liquid-liquid immiscibility increases with increasing a_{12} . This effect is due to the large size difference, and the opposite trend is more usual as shown with the mixtures of equal-sized hard cores of Sections 5.1.5-5.1.10.

Although strong solute-solvent attractive interactions are necessary in order to obtain a substantial liquid-liquid miscibility gap in the mixtures of point particles and hard cores, size considerations also proved crucial. In this chapter calculations were performed for mixtures of small (1) and large (2) hard cores with $a_{11}=0$ and $a_{12}=a_{22}/2$ and

with different values of the diameter ratio d_1/d_2 . The extent of liquid-liquid coexistence is greatest at maximal size differences, $d_1/d_2=0$, and the upper critical solution temperature falls as the size difference decreases until the solvent and solute are of equal size $d_1/d_2=1$ and no liquid-liquid immiscibility is present. The above trend can be understood in terms of an increase in the effective attractions between the larger spheres, brought about by the presence of the smaller spheres. This is consistent with the existence of "gas-gas immiscibility" in systems with $a_{11}=0$, $a_{12}=a_{22}/2$ and $d_1/d_2<0.5$ (Fig. 5.13), with an increase in the critical pressure and temperature as more of the smaller spheres are added. The mechanism of liquid-liquid phase separation involves large numbers of smaller spheres interposing themselves between some of the larger spheres enhancing their attractions to form a dense phase, leaving behind a less dense phase richer in larger spheres. Hence, the liquid phase which is richer in smaller spheres is much denser than the other coexisting liquid phase which is richer in the larger spheres (see Fig. 5.15, and note that here l_1 of Fig. 5.12(a) is now the phase on the right).

Therefore, the results for systems with large size differences indicate that the extent of liquid-liquid immiscibility increases both with increasing a_{12} and with increasing size difference, due to the enhanced effective attractions between the larger particles. The existence of liquid-liquid equilibria in the phase diagrams of these mixtures is in itself very interesting. Furthermore, the

experimental upper consolute boundaries for the zwitterionic surfactant-water systems described in Chapter 8 follow the trend predicted by the calculations: the larger the solute-to-solvent size ratio the greater the liquid-liquid miscibility gap.

Finally, it is worth mentioning the results of computer simulations for mixtures of different-sized particles. Calculations for binary mixtures of equal-sized molecules with different attractive interactions have been reported [55],[56],[57]. Gierycz et al. have carried out molecular dynamics simulations of binary mixtures of Lennard-Jones fluids with differing component sizes and attractive interactions [58],[59]. The studies were for model mixtures with diameter ratios of $d_2/d_1=1$, 2, and 3. Equimolar mixtures with $d_2/d_1=1.2$ and 1.3 have also been investigated by Schoen and Hoheisel [60]. For these systems it appears that, leaving the attractive interactions unchanged, the small increase in size difference strengthens the stability of the binary mixture. Furthermore, in certain cases the mixtures of particles of unlike size exhibited "gas-gas" phase separation. However, little attention has been given in the literature to larger size ratios, and an interesting line of future research could involve computer simulations for mixtures with large size differences.

CHAPTER 6

VAN DER WAALS MIXTURES

In Chapter 4 the equation of state proposed by Mansoori et al. for mixtures of hard spheres [11] was used to calculate the critical lines and phase equilibria of binary mixtures of hard cores and point particles ($d_1=0$). The resulting equations for the critical lines were of very high order in reduced density and composition, and consequently, many roots satisfied the equations. Some of these roots were found to be unstable and were discarded. However, in certain cases physically absurd results were obtained from stable roots. For example, densities in excess of hard sphere close-packing were obtained at very high pressures.

The van der Waals equation can also be used to calculate a fluid mixture's phase equilibria. Although the equation gives only a qualitative description of the mixture's properties, it virtually never yields physically absurd results. Hence by comparing the critical lines and phase equilibria of the hard core mixture with the results for a corresponding van der Waals mixture, we can verify the hard core results.

Van Konynenburg and Scott have determined phase boundaries for binary mixtures of van der Waals molecules [5]. Most of the calculations were for the case of equal-sized molecules ($d_1=d_2$), but they also gave results for a diameter ratio of $d_2/d_1=1.26$.

In the following discussion the van der Waals equation will be used to determine the critical lines and phase equilibria for a binary mixture of van der Waals molecules and point particles ($d_1=0$). A comparison of the resulting phase behaviour with that obtained for a binary mixture of point particles and hard cores (Section 4.8.2) will point out the similarities and differences between the two systems. Furthermore, such a comparison will enable us to establish which feature, if any, of the Mansoori phase equilibria is an artefact of the hard sphere equation.

6.1 VAN DER WAALS EQUATION WITH $d_1=0$

The van der Waals equation of state is

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

The molecule's intrinsic size and the attractive forces between the molecules are described by the parameters b and a respectively. For a binary mixture van der Waals replaced a and b by

$$a = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2$$

$$b = b_{11}x_1^2 + 2b_{12}x_1x_2 + b_{22}x_2^2$$

The Lorentz combining rule is chosen for b_{12}

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

and a_{12} can be related to a_{11} and a_{22} by the arithmetic mean

$$a_{12} = (a_{11} + a_{22}) / 2$$

For a binary mixture of van der Waals molecules and point particles the parameter b is

$$b_{11} = 0, \quad b_{12} = b_{22}/8, \quad b_{22} = \frac{2}{3}\pi L d_2^3$$

$$b = \frac{2}{8}x_1x_2b_{22} + b_{22}x_2^2$$

The mixture's pressure is expressed in terms of the reduced density of the van der Waals molecules. N.B. to avoid confusion with the van der Waals b , b' is used for the parameter b of the previous chapters.

$$P = \frac{\eta}{b'x_2[1-\eta(1+3x_2)]} RT - \frac{a\eta^2}{(b'x_2)^2}$$

$$b' = \pi L d_2^3/6, \quad \eta = x_2 b' / V_m$$

6.1.1 The Free Energy

In order to calculate the critical lines for such a van der Waals mixture an expression for the Helmholtz free energy is required. The free energy is obtained from the pressure by integration.

$$\left(\frac{\partial A}{\partial V} \right)_T = -P, \quad A = - \int P dV$$

$$A_m = Lx_1\mu_1^0 + Lx_2\mu_2^0 + x_1RT \ln(x_1RT/V_m) + x_2RT \ln(x_2RT/V_m) - RT \\ - RT \ln[1-\eta(1+3x_2)] - (a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2) \eta / (b'x_2)$$

$$\mu_1^0 = -kT \ln[(2\pi m_1 kT/h^2)^{3/2} kT], \quad \mu_2^0 = -kT \ln[(2\pi m_2 kT/h^2)^{3/2} kT]$$

6.1.2 System With $a_{11}=0$, $a_{12}=a_{22}/2$, And $a_{22}>0$

As with the binary mixture of point particles and hard cores described in Section 4.8.2, the attractive interactions between the points and the van der Waals molecules are taken as the arithmetic mean, $a_{12}=a_{22}/2$. The van der Waals equation of state is expressed in its reduced form. The pressure and temperature are reduced with respect to the pure van der Waals fluid, and the composition x_2 and reduced density η represent the van der Waals molecules.

$$a_{11} = 0, \quad a_{12} = (a_{11} + a_{22})/2 = a_{22}/2, \quad a_{22} > 0$$

$$P_r = \frac{\eta T_r}{\eta_{c,2} Z_{c,2} x_2 [1 - \eta (1 + 3x_2)]} - \frac{A_{c,2} \eta^2}{\eta_{c,2} Z_{c,2} x_2}, \quad \eta = \frac{\pi N_2 d_2^3}{6V}$$

$$P_r = P/P_{c,2}, \quad T_r = T/T_{c,2}$$

$$\eta_{c,2} = 1/12, \quad A_{c,2} = 13.5, \quad Z_{c,2} = 0.375$$

6.1.2.1 The Critical Lines -

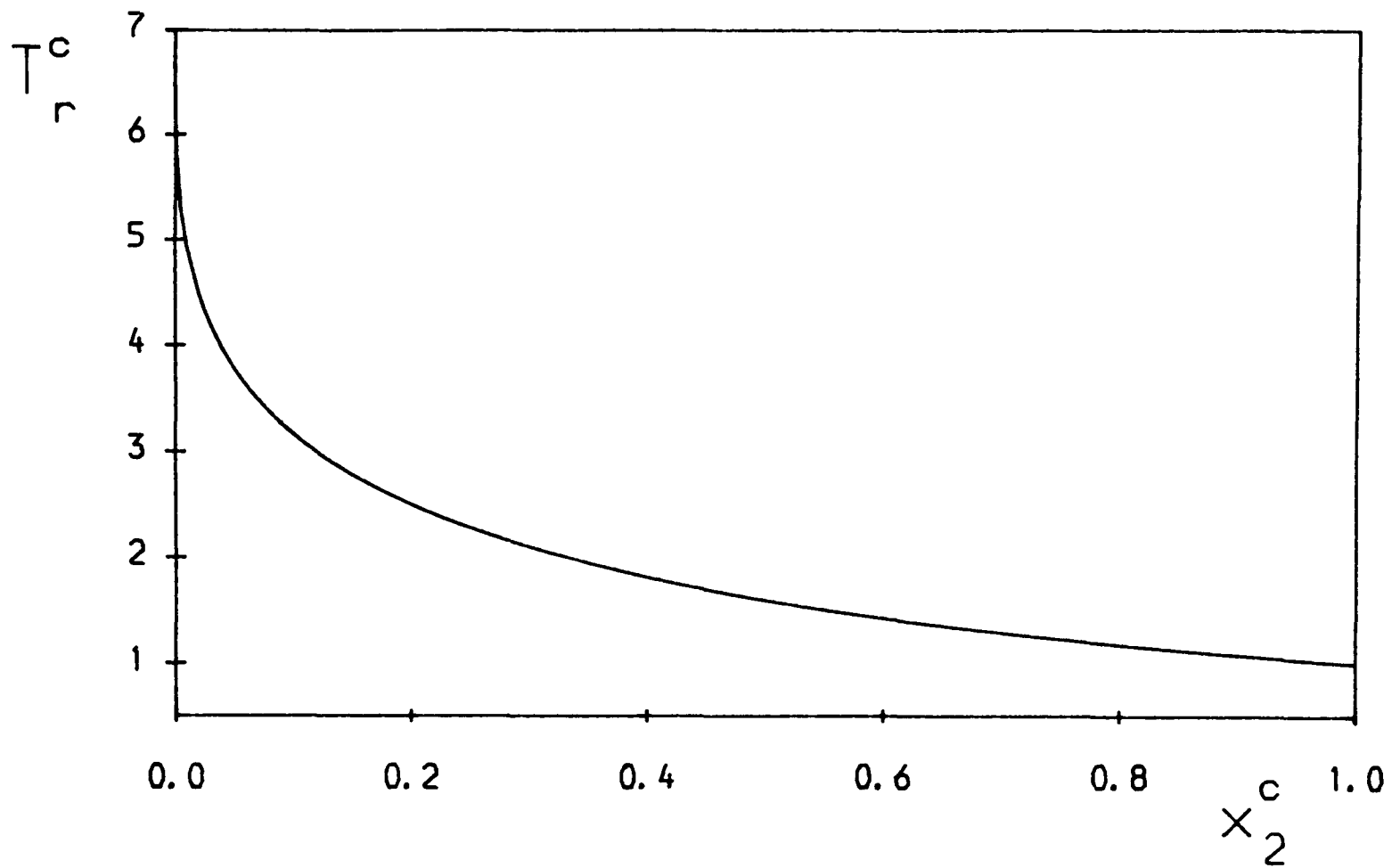
The conditions for a critical point are expressed in terms of the Helmholtz free energy as

$$A_{2v} A_{2x} - A_{vx}^2 = 0$$

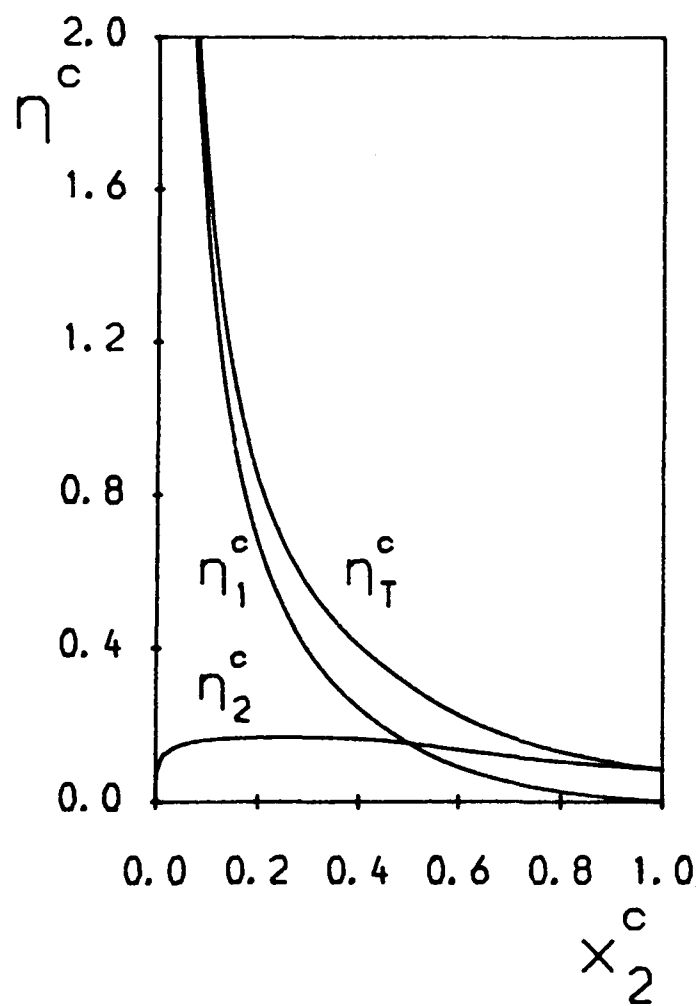
$$A_{3v} A_{2x}^2 - 3A_{2vx} A_{vx} A_{2x} + 3A_{v2x} A_{vx}^2 - A_{3x} A_{2v} A_{vx} = 0$$

The two conditions were solved simultaneously to eliminate the temperature, and the resulting equation was used to compute the reduced critical density at a given composition. The procedure was described in detail when the hard core critical lines were calculated (Section 4.6). As with the system of point particles and hard cores, two critical lines were obtained. The van der Waals results are qualitatively analogous to the hard cores results, and it will be clear from the phase diagrams that one line is associated with gas-liquid critical points and the other line represents liquid-liquid critical points.

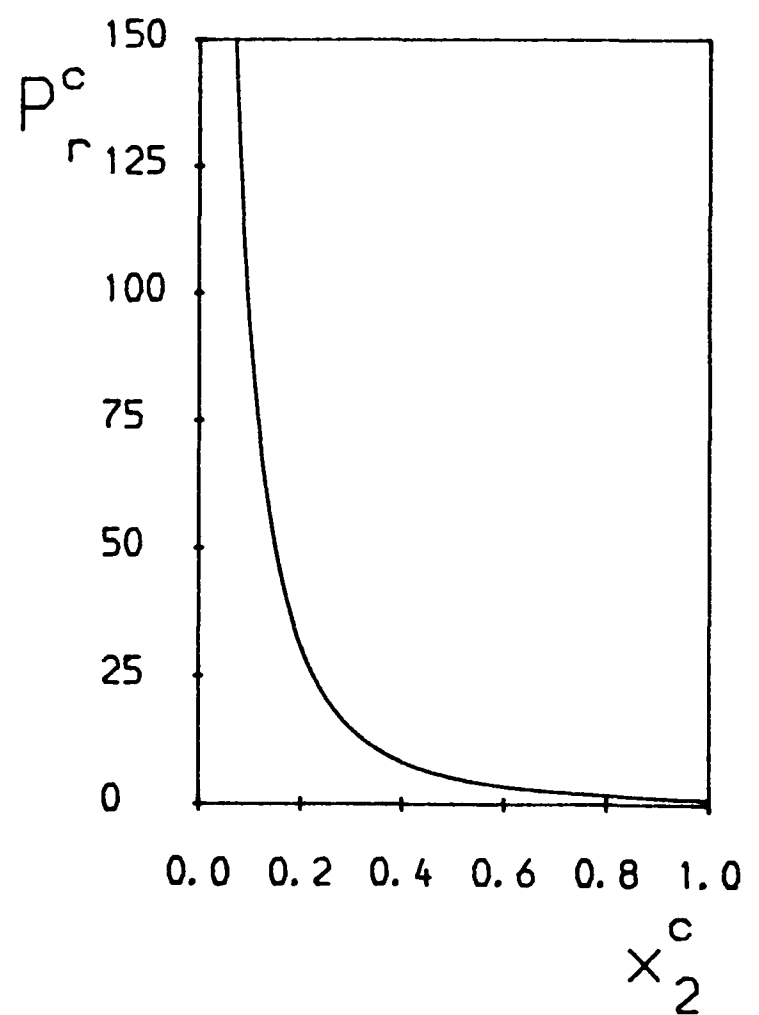
The gas-liquid critical temperature, pressure and densities of components 1 (points) and 2 (van der Waals molecules) are plotted against composition in Fig. 6.1(a-c). The gas-liquid critical points show an increase in the critical temperature with decreasing mole fraction, accompanied by an increase in the reduced critical density of component 1. The mixture of van der Waals molecules and point particles also appears to have a limiting critical temperature of $T_r=6.75$ ($A_c=2, T_c=13.5/2$) at zero composition, $x_2=0$. It will be clear from an investigation of the PTx surface that a portion of the gas-liquid critical line is metastable; the gas-liquid critical point ends at an upper critical end point, UCEP, reappearing again at a lower critical end point, LCEP. This behaviour is due to the dominating influence of the liquid-liquid immiscibility at moderate temperatures.



(a)

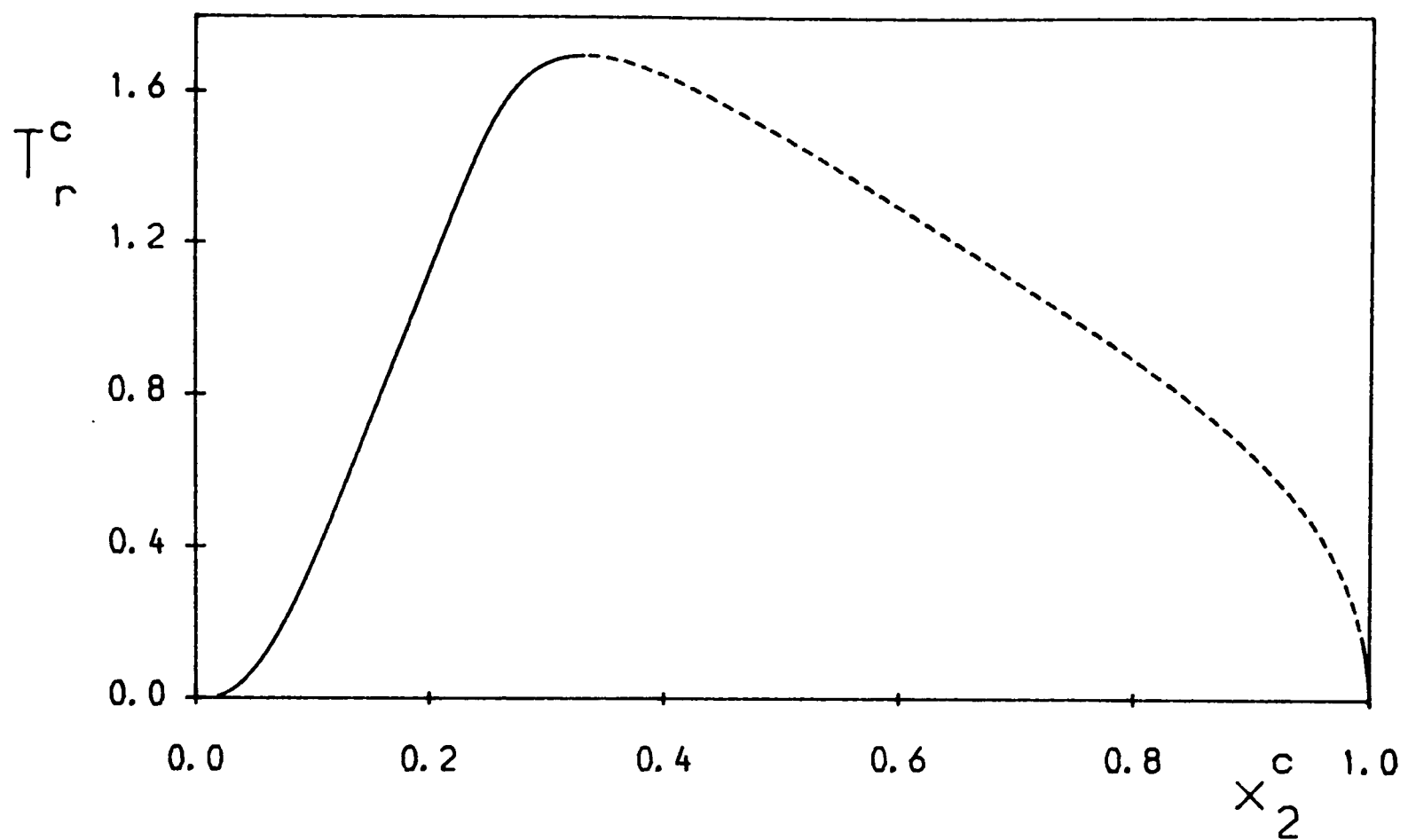


(b)

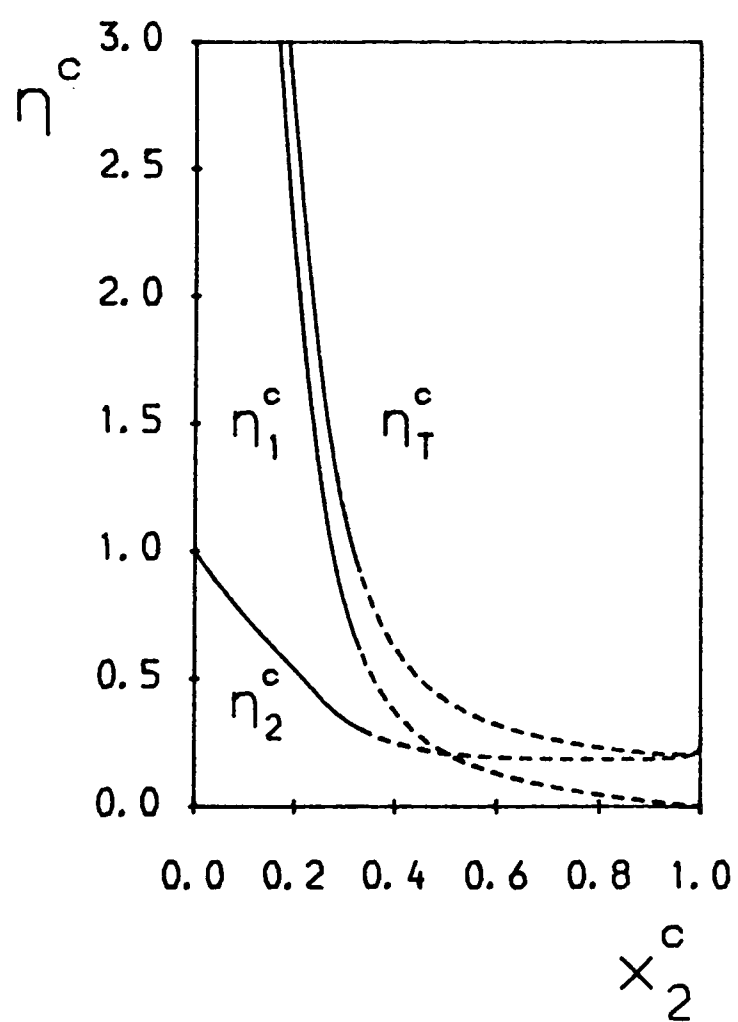


(c)

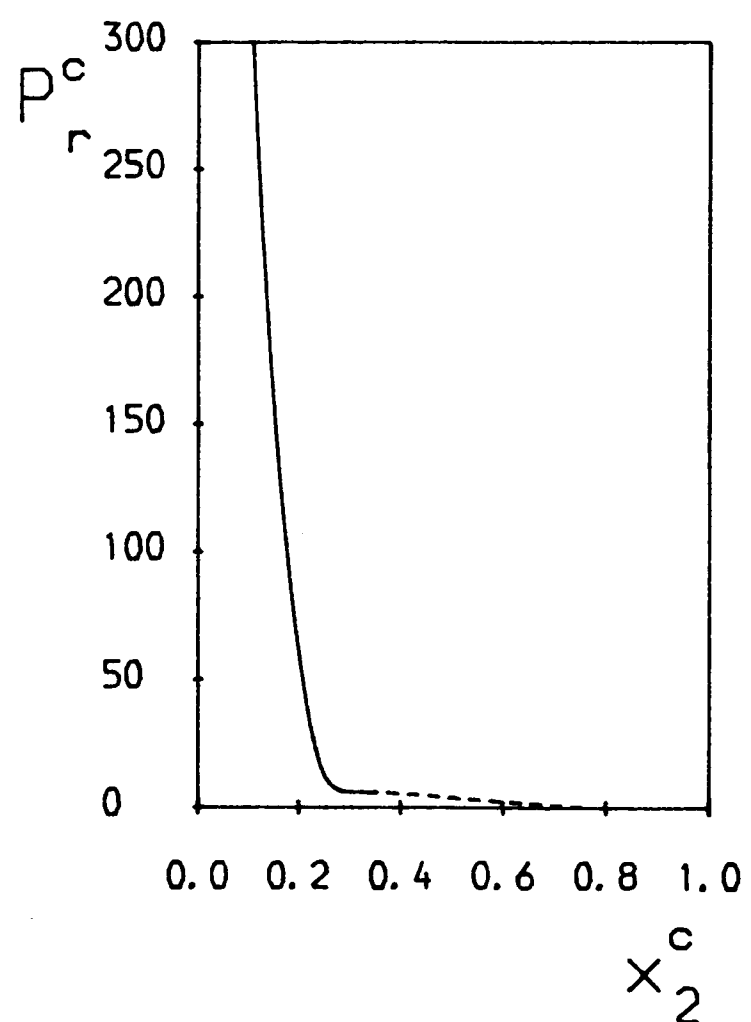
Fig. 6.1 Gas-liquid critical line for a mixture of points and van der Waals molecules with $a_{11}=0$ and $a_{12}=a_{22}/2$.



(a)



(b)



(c)

Fig. 6.2 Liquid-liquid critical line for a mixture of points and van der Waals molecules with $a_{11}=0$ and $a_{12}=a_{22}/2$.

The liquid-liquid critical line is represented graphically in Fig. 6.2(a-c). When the mole fraction is zero, the reduced critical temperature is also zero and the reduced critical pressure tends to infinity. Instability for the critical line (dashed) is seen above $x_2=0.33$ when the sign of the fourth derivative of the Gibbs free energy with respect to composition becomes negative. The critical pressure becomes negative at compositions above about $x_2=0.76$, but the critical line becomes metastable long before then by meeting an upper critical end point. This is established from a study of the isothermal pressure-composition slices of the PTx surface.

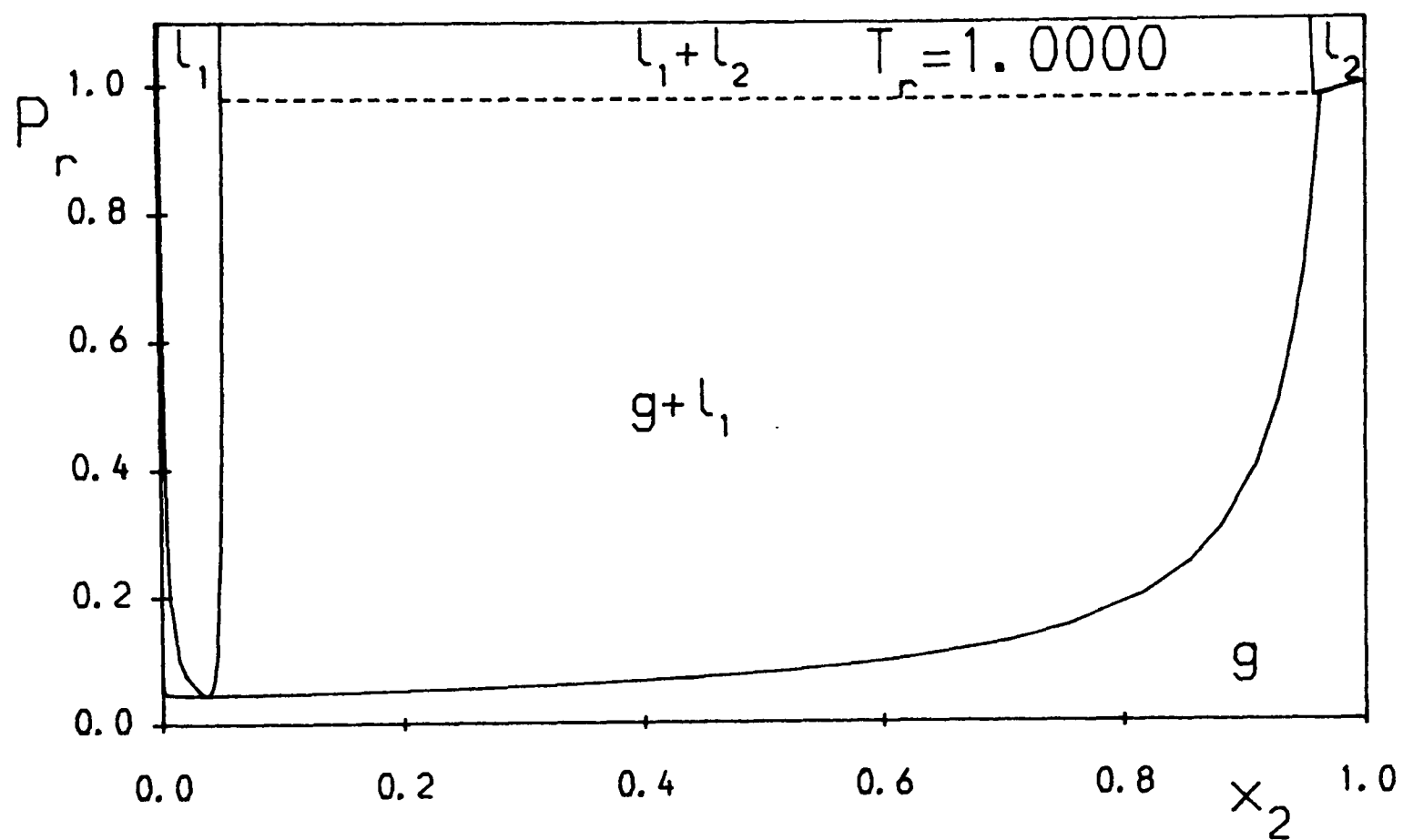
6.1.2.2 Pressure-Composition Phase Diagrams -

The van der Waals system's pressure-composition phase diagrams were obtained as described in Section 4.7. The activities for a mixture of points and van der Waals molecules with $a_{11}=0$ and $a_{12}=a_{22}/2$ are

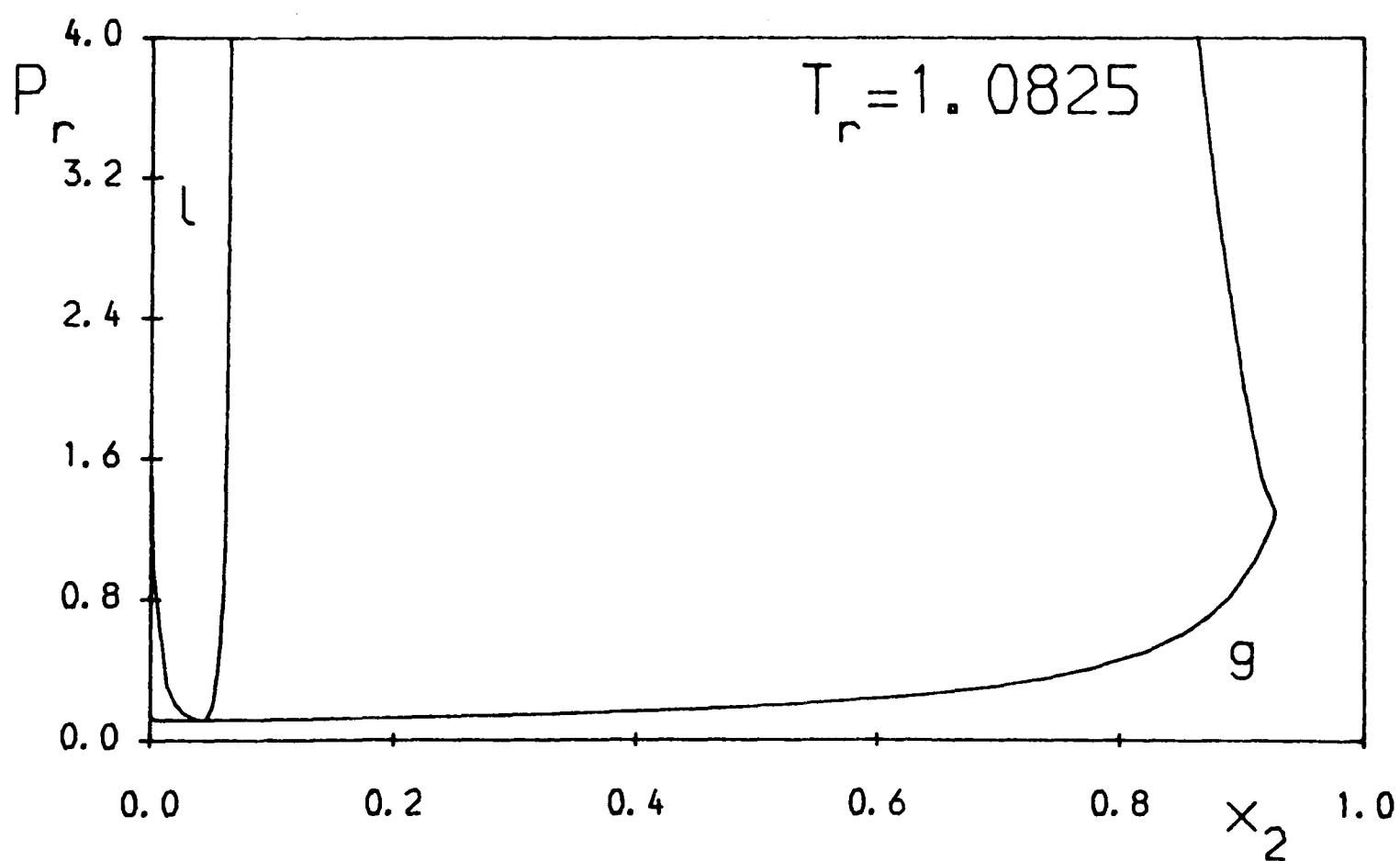
$$\ln \lambda_1 = (\mu_1 - \mu_1^\circ) / RT = \ln(\eta) + \ln[(1-x_2)/x_2] - \ln[1-\eta(1+3x_2)] - 3x_2\eta/[1-\eta(1+3x_2)] - A_c\eta/T_r$$

$$\ln \lambda_2 = (\mu_2 - \mu_2^\circ) / RT = \ln(\eta) - \ln[1-\eta(1+3x_2)] + \frac{1+6x_2-3x_2^2}{x_2[1-\eta(1+3x_2)]} - \frac{(1+x_2)A_c\eta}{x_2T_r}$$

and these equations are then used to calculate the isothermal pressure-composition phase diagrams.

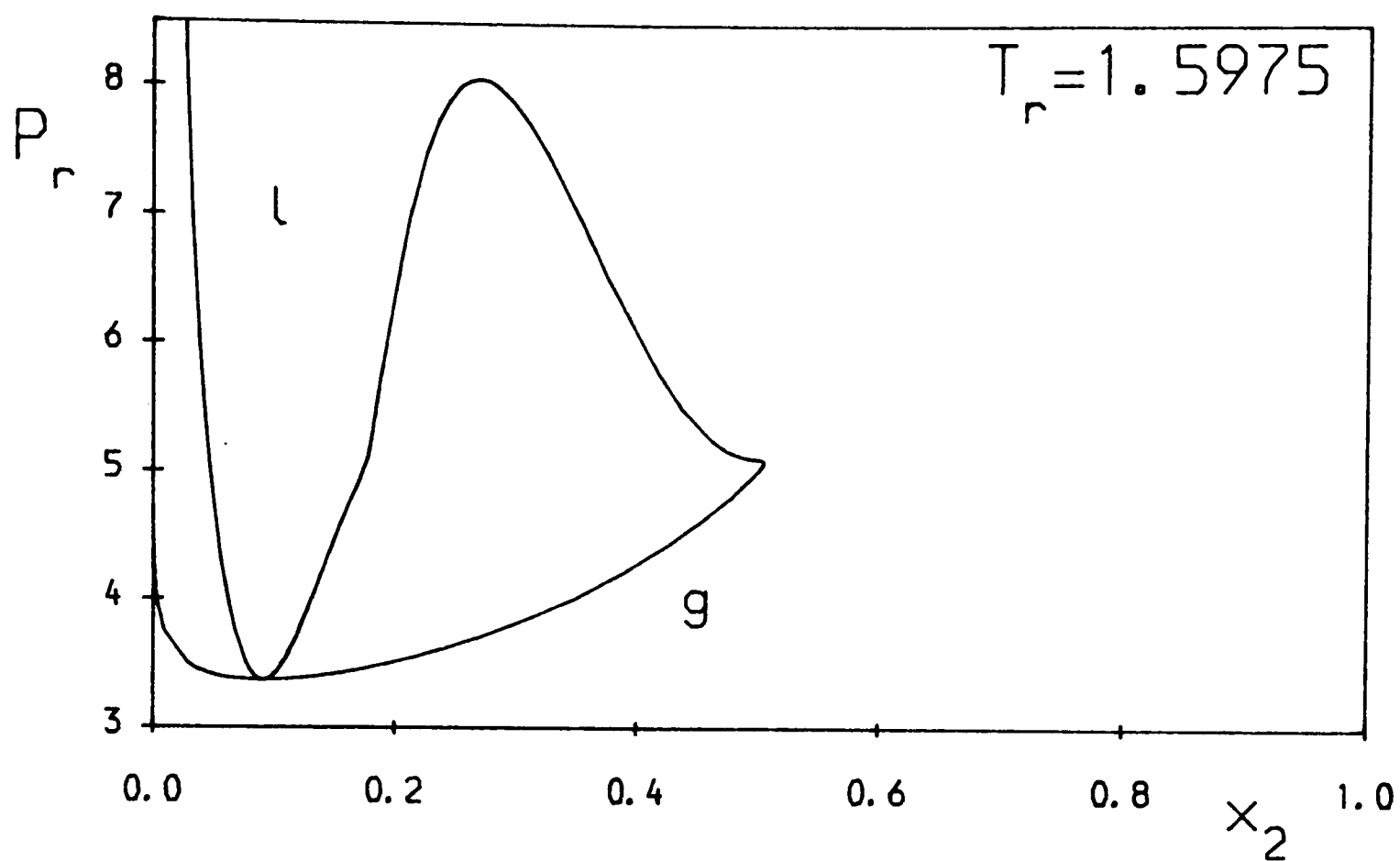


(a)

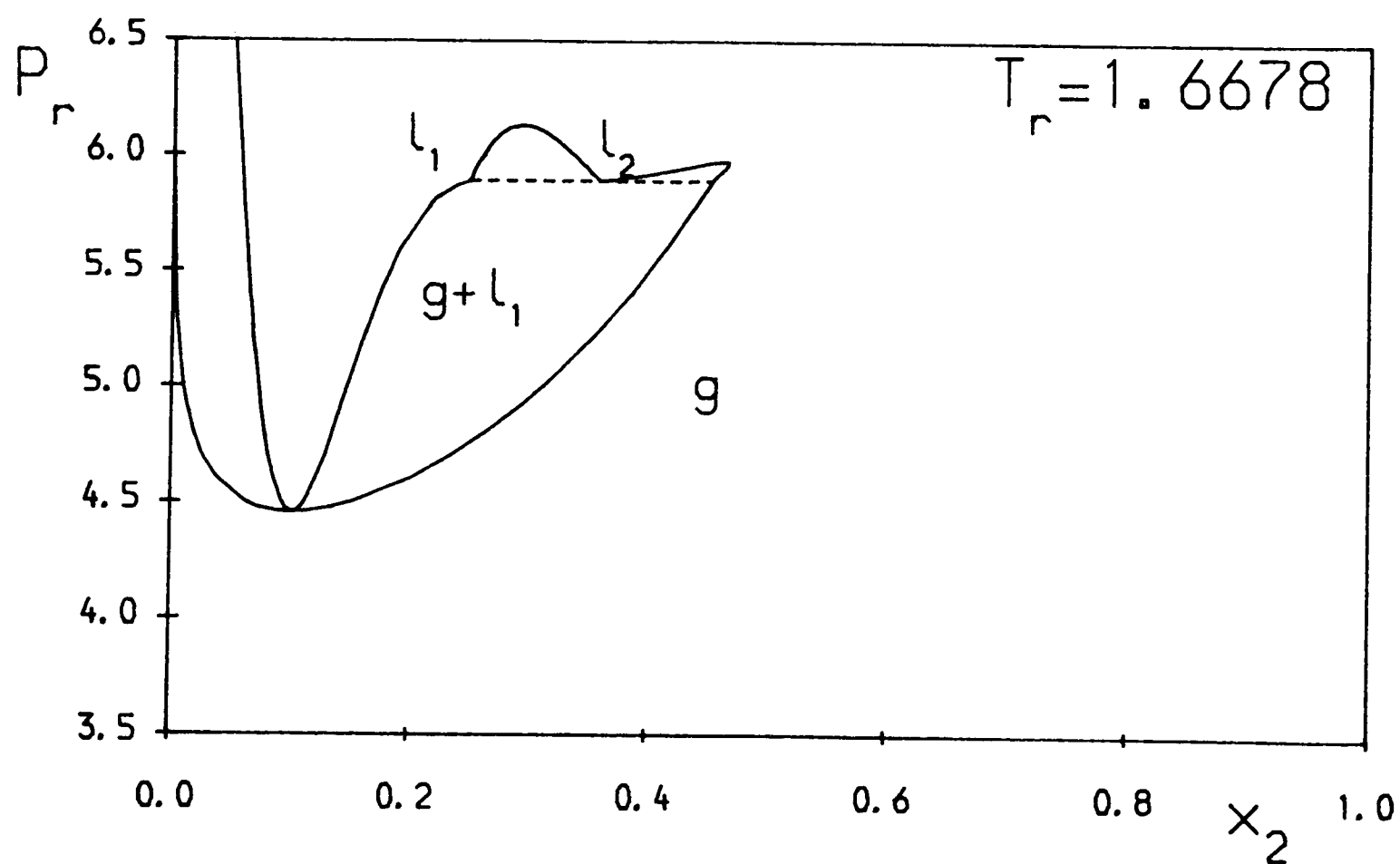


(b)

Fig. 6.3 Isothermal Px phase diagrams for the mixture of points and van der Waals molecules with $a_{11}=0$ and $a_{12}=a_{22}/2$.

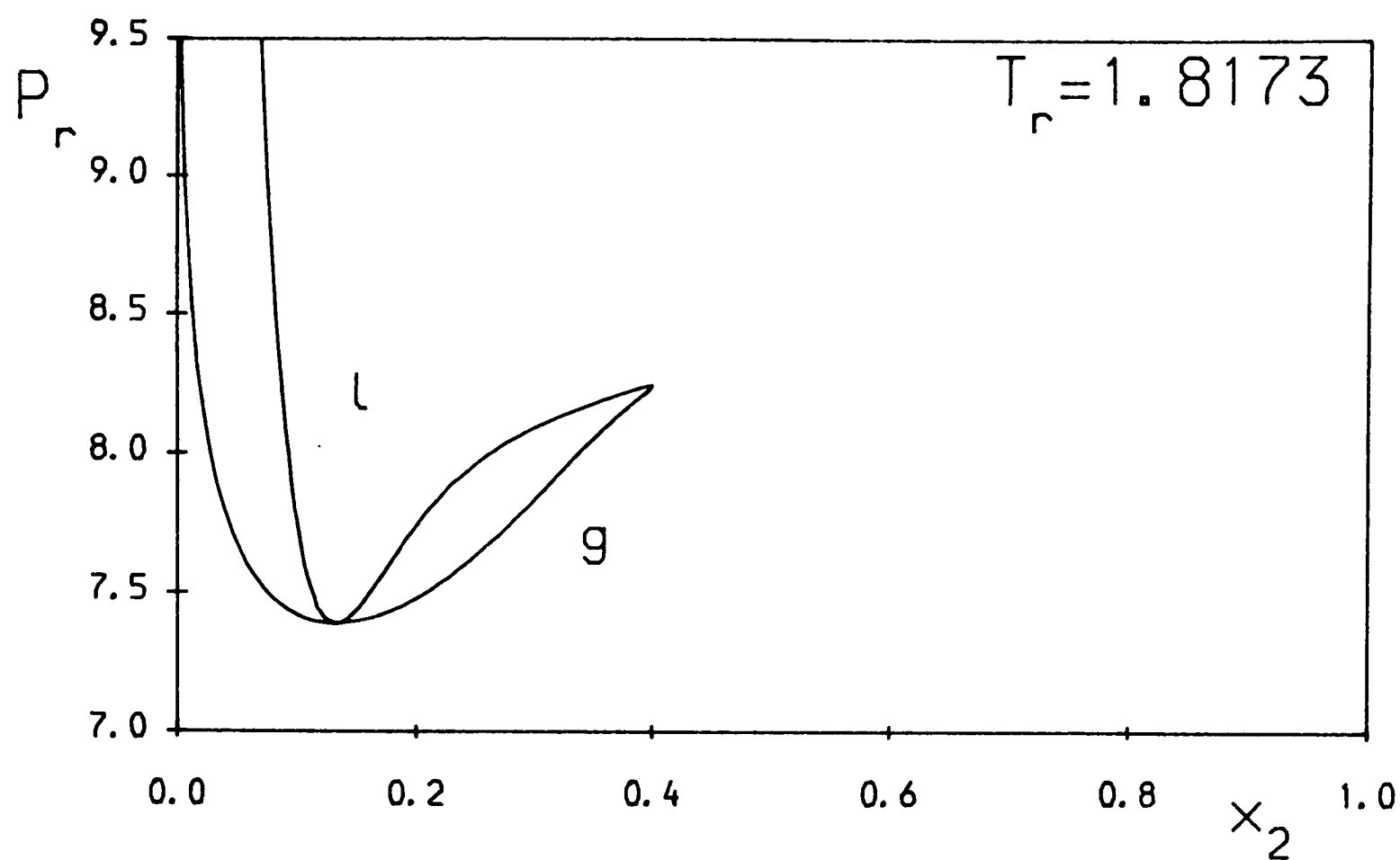


(c)

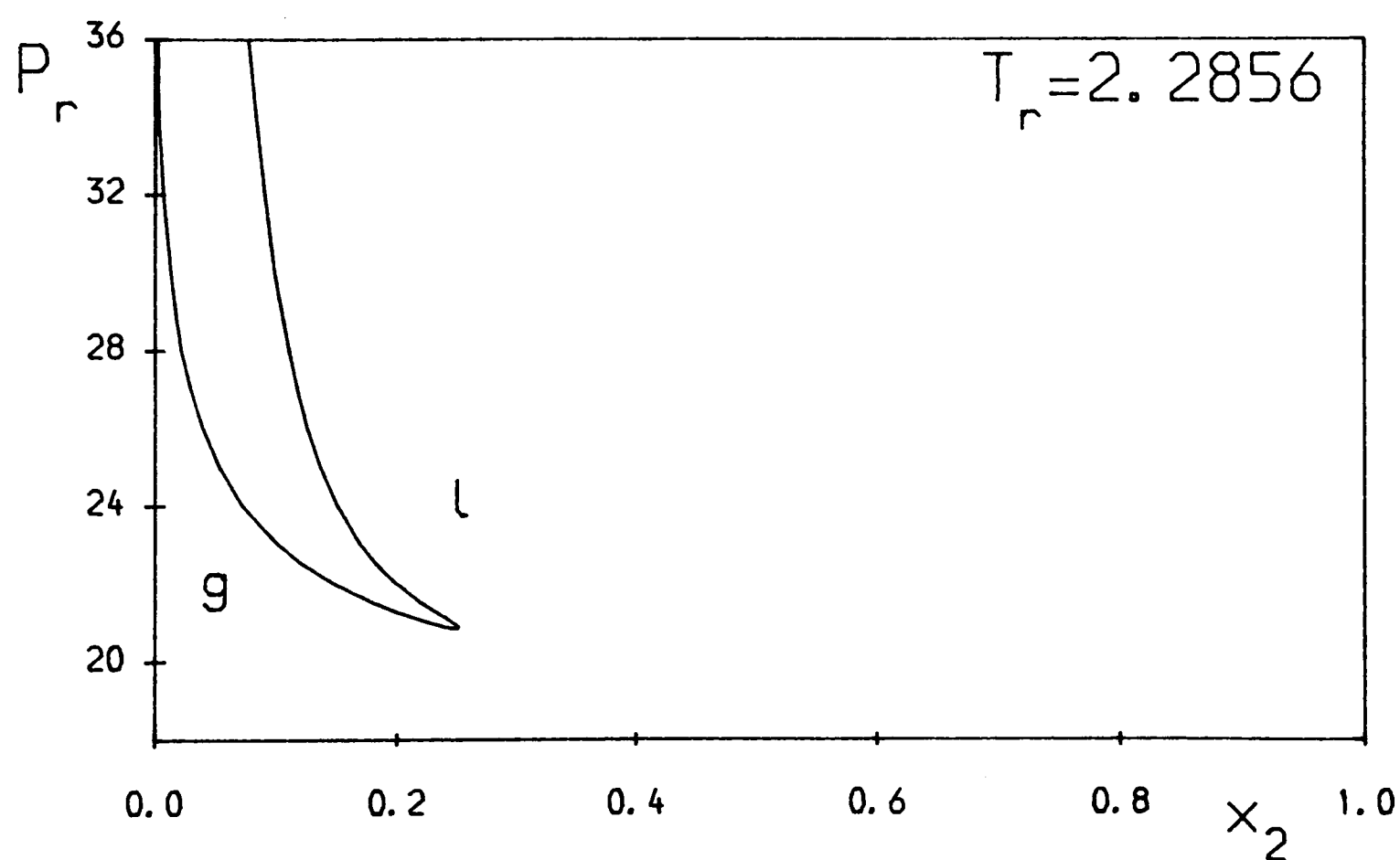


(d)

Fig. 6.3(cont'd)Px phase diagrams for the mixture of points and van der Waals molecules, $a_{11}=0$ and $a_{12}=a_{22}/2$.



(e)



(f)

Fig. 6.3(cont'd)Px phase diagrams for the mixture of points and van der Waals molecules, $a_{11}=0$ and $a_{12}=a_{22}/2$.

The P_x phase diagrams are shown in Fig. 6.3(a-f). At temperatures below $T_r=1.0$ the liquid-liquid phase coexistence dominates the phase behaviour over a relatively large pressure range so that most of the phase diagram represents a region of liquid-liquid immiscibility. The phase diagram at a reduced temperature of $T_r=1.0$ is depicted in Fig. 6.3(a); both gas-liquid and liquid-liquid coexistence are present, and a negative azeotrope at a composition of about $x_2=0.04$ can also be seen. The dotted line indicates the point of liquid-liquid-gas coexistence. The liquid-liquid immiscibility disappears at a pressure of about $P_r=87.96$, and for scaling reasons this liquid-liquid critical point is not shown.

Just above a temperature of $T_r=1.0$, the gas-liquid critical line ends at an UCEP when it meets the liquid-liquid-gas coexistence line. Above this temperature no gas-liquid critical points are present. Fig. 6.3(b) represents a P_x phase diagram at a temperature of $T_r=1.0825$ with the liquid-liquid critical point at a pressure of $P_r=70.49$ (it is not shown). At a temperature of $T_r=1.5975$ (Fig. 6.3(c)) the liquid-liquid critical point has an even lower pressure, the immiscibility disappearing at a value of $P_r=8.07$.

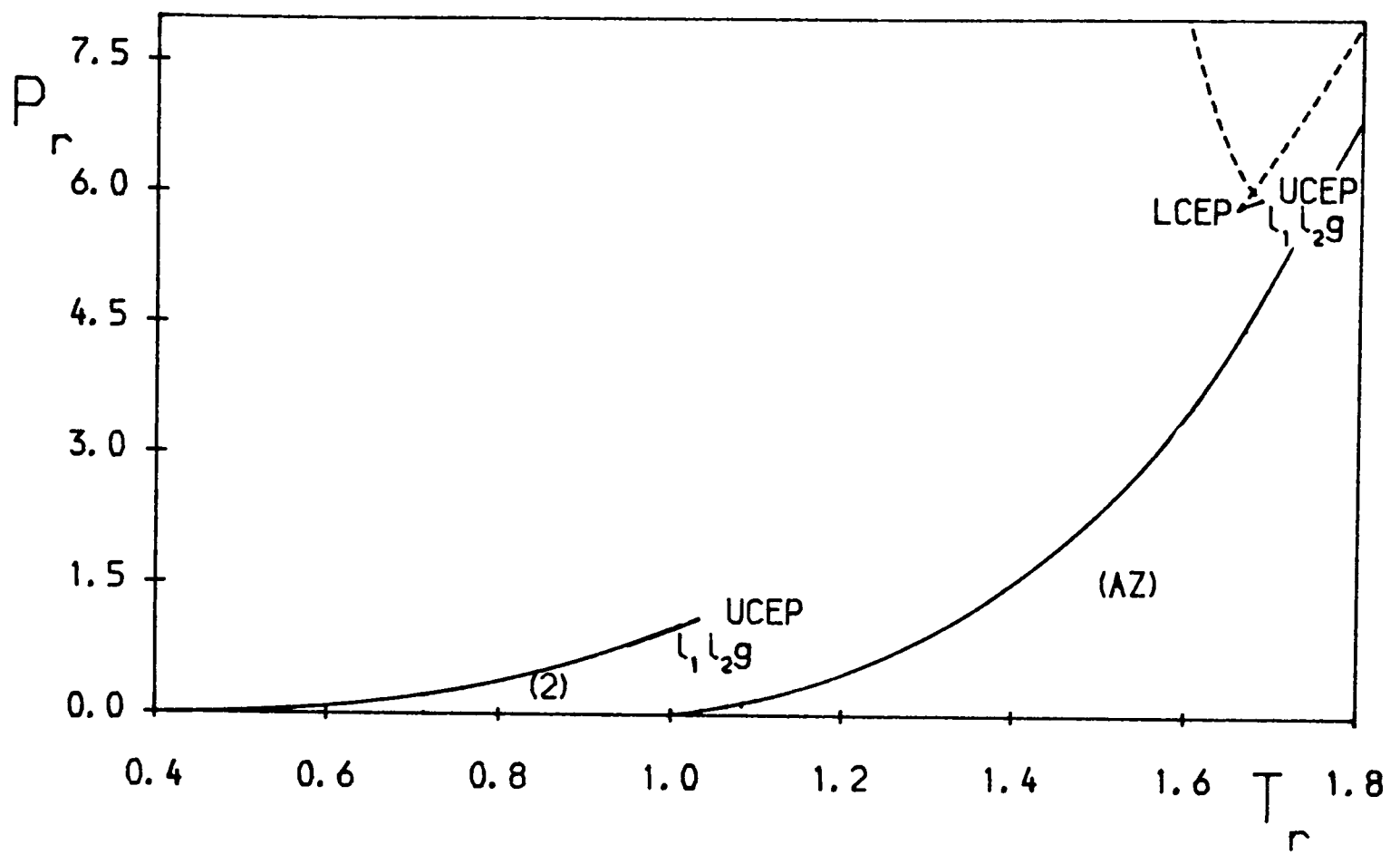
When the temperature is increased to $T_r=1.6678$, gas-liquid coexistence has reappeared above a LCEP so that both gas-liquid and liquid-liquid phase coexistence are again present (Fig. 6.3(d)). Eventually liquid-liquid coexistence disappears when the critical point meets the

three phase line at an UCEP. Above this UCEP only gas-liquid phase coexistence is seen as in Fig. 6.3(e) representing a temperature of $T_r=1.8173$. A further increase in temperature sees the disappearance of the azeotrope (Fig. 6.3(f)).

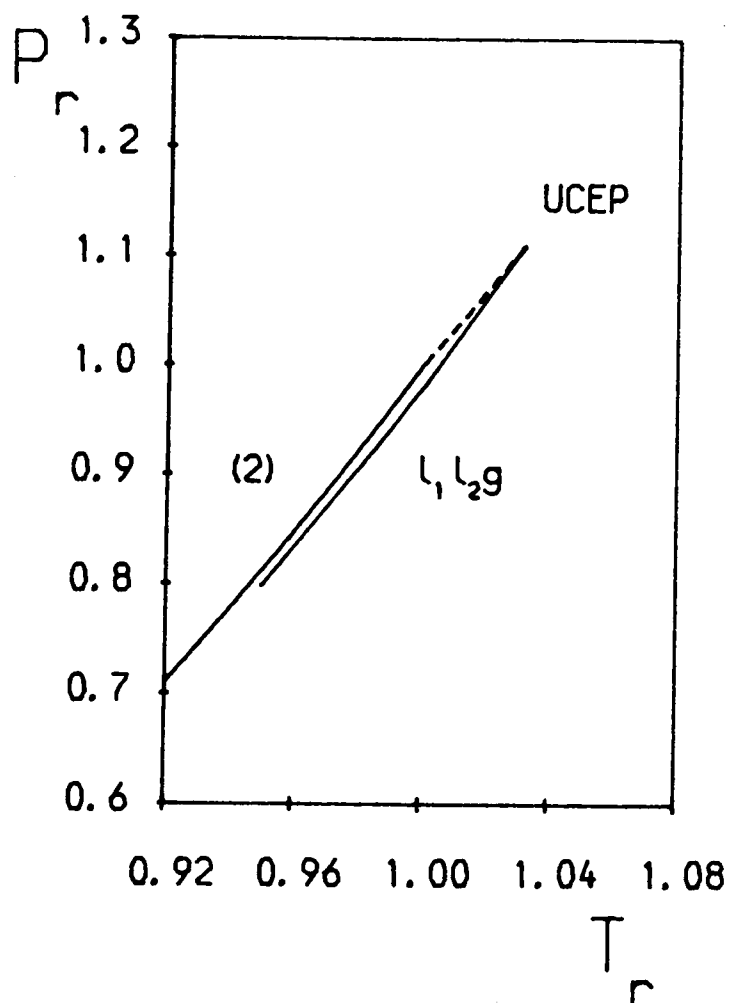
6.1.2.3 Pressure-Temperature Projection -

The pressure-temperature projection of the PTx surface for the system of point particles and van der Waals molecules is depicted in Fig. 6.4(a). The vapour pressure curve for the pure van der Waals fluid is represented (denoted 2) together with the gas-liquid and liquid-liquid critical lines (dotted). The gas-liquid critical line disappears at an UCEP (see enlargement Fig. 6.4(b)) and then reappears at a LCEP. The liquid-liquid critical line ends at an UCEP when it meets the three phase line (solid line). It was mentioned earlier that the system has a limiting critical temperature at zero composition. Fig. 6.4(c) confirms this point with the critical temperature tending to $T_r=13.5/2=6.75$ as the pressure becomes infinite.

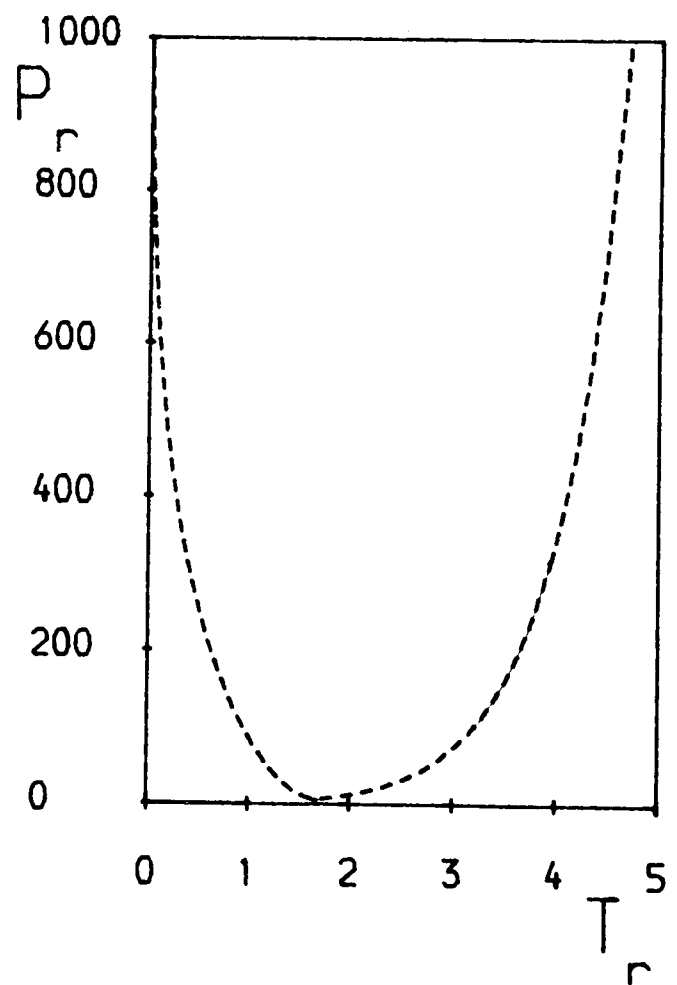
The conclusion we can draw from these results is that the phase behaviour of a system of point particles and van der Waals molecules is very similar to the behaviour of a system of points and hard cores. The main difference seems to be in the extent of liquid-liquid immiscibility.



(a)



(b)



(c)

Fig. 6.4 PT projection for the mixture of points and van der Waals molecules with $a_{11}=0$ and $a_{12}=a_{22}/2$.

In the case of the point-hard core phase diagrams of Fig. 4.14(a-e), liquid-liquid coexistence has disappeared before the appearance of gas-liquid critical points. This is not the case with the analogous van der Waals system which retains its liquid-liquid coexistence up to a reduced temperature of about $T_r=1.67$. Hence, the van der Waals mixture's phase diagrams are slightly more complicated than those obtained using the hard core equation.

6.2 VAN DER WAALS CONFIGURATIONAL INTEGRAL

The configurational integral offers a route to a van der Waals equation of state for a binary mixture of point particles and van der Waals molecules. The configurational integral can be expressed as

$$Q = \frac{1}{N_1! N_2!} \int_V d\mathbf{r}^{N_2} e^{-U_2/kT} \left[\int_{N_2 v} d\mathbf{r}^{N_1} e^{-(U_{12}+U_{11})/kT} = 0 \right. \\ \left. + \int_{V-N_2 v} d\mathbf{r}^{N_1} e^{-(U_{12}+U_{11})/kT} = V-N_2 v \right]$$

$$N_2 v : U_{11} = 0, U_{12} = \infty$$

$$V-N_2 v : U_{11} = 0, U_{12} = 0$$

The configurational integral for a pure van der Waals fluid is

$$Q_2 = \frac{1}{N_2!} \int_V d\mathbf{r}^{N_2} e^{-U_2/kT}$$

6.2.1 The Equation Of State

The equation of state can be obtained via the configurational free energy, A' , as follows

$$Q = \frac{1}{N_1!} (V - N_2 v)^{N_1} Q_2, \quad A' = -kT \ln Q, \quad \left(\frac{\partial A'}{\partial V} \right)_T = -P$$

$$\frac{PV}{kT} = \frac{N_1}{(1 - N_2 v/V)} + \frac{N_2}{1 - 4\eta}$$

$$Z = \frac{1 + \eta(3x_2 - 4)}{(1 - \eta)(1 - 4\eta)}, \quad \eta = \frac{N_2 v}{V}$$

This equation of state is different from the van der Waals equation used at the beginning of this chapter because the latter equation depends on an approximate expression of b for a binary mixture. Hence, the equation of state obtained from the configurational integral is the "exact" van der Waals equation of state for a binary mixture of point particles and van der Waals molecules.

After adding the van der Waals attractions with $a_{11}=0$ and $a_{12}=a_{22}/2$, the reduced form of the equation of state is

$$a_{11} = 0, \quad a_{12} = (a_{11} + a_{22})/2 = a_{22}/2, \quad a_{22} > 0$$

$$P_r = \frac{\eta[1 + (3x_2 - 4)\eta]T_r}{\eta_{c,2}Z_{c,2}x_2(1 - \eta)(1 - 4\eta)} - \frac{A_{c,2}\eta^2}{\eta_{c,2}Z_{c,2}x_2}, \quad \eta = \frac{\pi N_2 d_2^3}{6V}$$

$$P_r = P/P_{c,2}, \quad T_r = T/T_{c,2}$$

$$\eta_{c,2} = 1/12, \quad A_{c,2} = 13.5, \quad Z_{c,2} = 0.375$$

6.2.2 The Free Energy

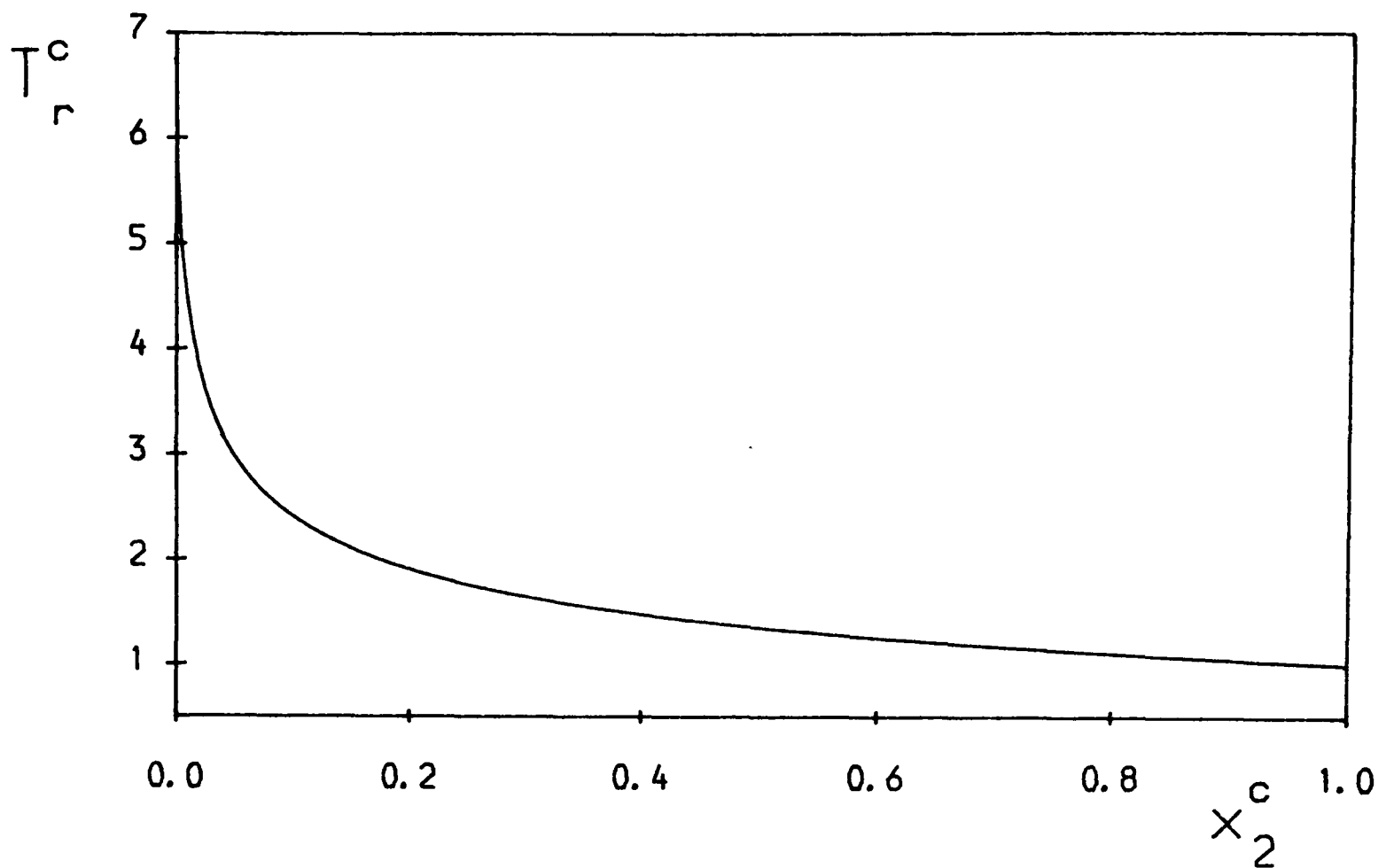
The calculation of the critical lines requires the Helmholtz free energy. By integrating the expression for the pressure obtained from the configurational integral with respect to the volume, the molar Helmholtz free energy for a mixture of points and van der Waals molecules is obtained.

$$A_m = Lx_1\mu_1^\circ + Lx_2\mu_2^\circ + x_1RT \ln(x_1RT/V_m) + x_2RT \ln(x_2RT/V_m) - RT \\ - x_1RT \ln(1-\eta) - x_2RT \ln(1-4\eta) - (a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2)\eta / (b'x_2)$$

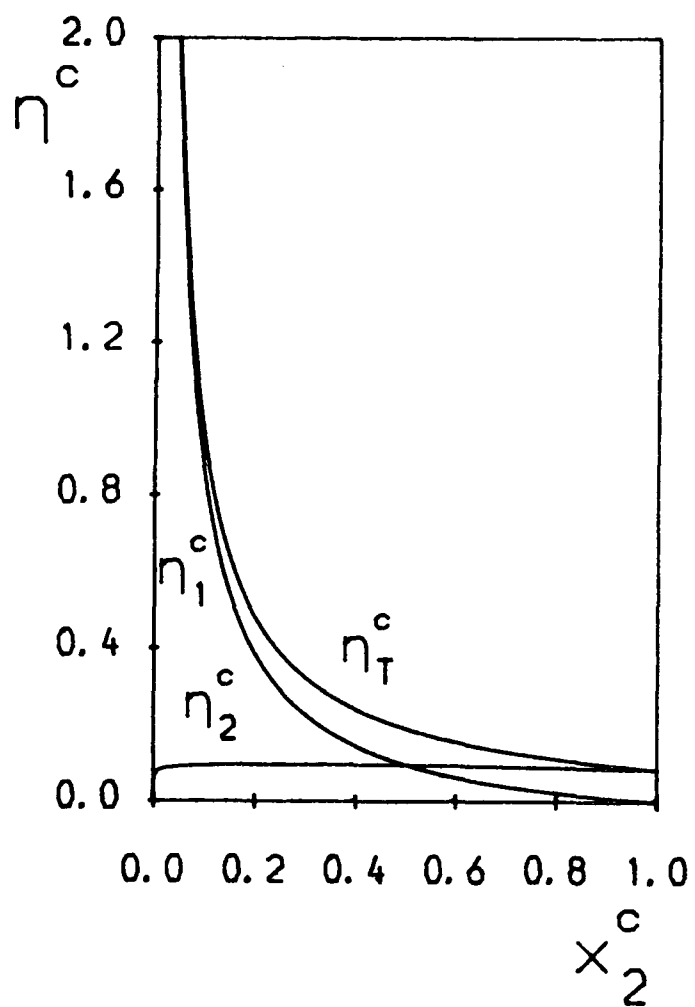
$$\mu_1^\circ = -kT \ln[(2\pi m_1 kT/h^2)^{3/2} kT] , \quad \mu_2^\circ = -kT \ln[(2\pi m_2 kT/h^2)^{3/2} kT]$$

6.2.3 The Critical Lines

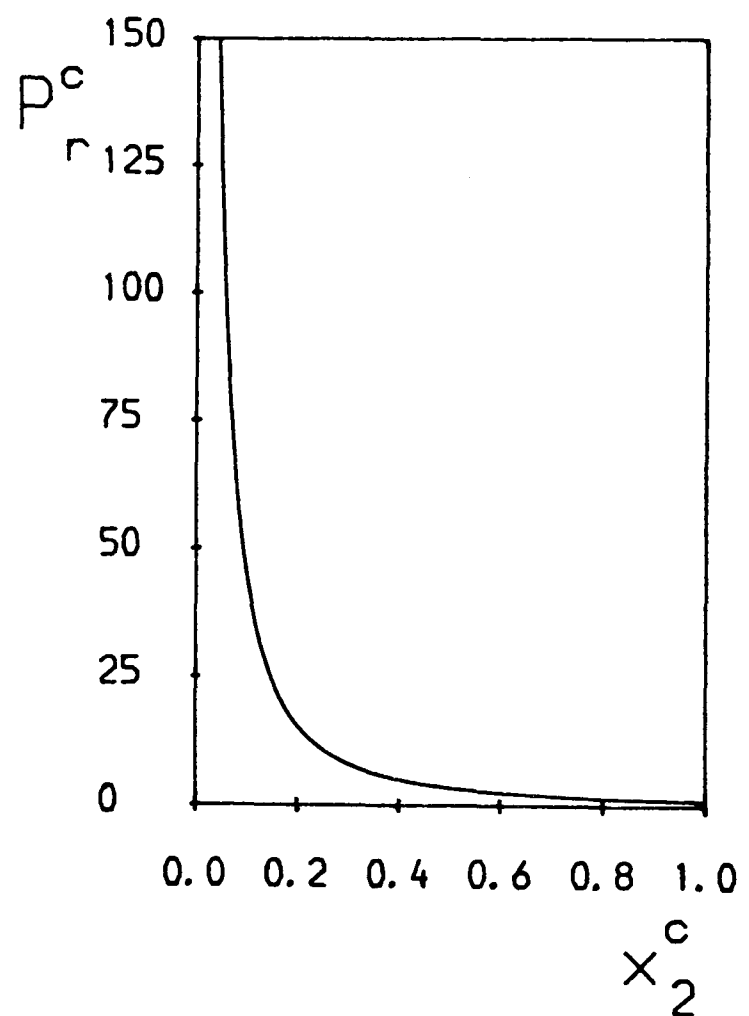
By using the conditions of criticality, the critical lines for this equation were calculated. Two critical lines were obtained. The gas-liquid critical line was very similar to the line obtained using the other van der Waals equation, the only notable difference being the lower values obtained for the reduced critical densities of component 2 (van der Waals molecules). The other critical line which normally represents the liquid-liquid roots appears to be unstable and, above a composition of about $x_2=0.1$, the roots yield negative critical pressures. Hence, the system does not show liquid-liquid coexistence.



(a)



(b)



(c)

Fig. 6.5 Gas-liquid critical line obtained for a mixture of points and van der Waals molecules using an equation derived from the configurational integral with $a_{11}=0$ and $a_{12}=a_{22}/2$.

The gas-liquid critical line is represented in Fig. 6.5(a-c), but the unstable "liquid-liquid" critical line is not shown. As before, the reduced critical temperature increases as the mole fraction decreases with a limiting critical temperature of $T_r = 13.5/2 = 6.75$ at zero composition.

6.2.4 The Px Phase Diagram And PT Projection

The activities for the van der Waals equation obtained from the configurational integral are determined by differentiating the free energy with respect to the number of molecules of each component, and the resulting equations are

$$\ln \lambda_1 = (\mu_1 - \mu_1^\circ) / RT = \ln(\eta) + \ln[(1-x_2)/x_2] - \ln(1-\eta) - A_c \eta / T_r$$

$$\ln \lambda_2 = (\mu_2 - \mu_2^\circ) / RT = \ln(\eta) + \frac{(1-x_2)\eta}{x_2(1-\eta)} + \frac{4\eta}{1-4\eta} - \ln(1-4\eta) - \frac{(1+x_2)A_c \eta}{x_2 T_r}$$

These expressions are then used to calculate the pressure-composition phase diagram at a reduced temperature of $T_r = 0.8000$ (see Fig. 6.6). As expected the phase diagram does not show any liquid-liquid coexistence, and the only special feature is the presence of the negative azeotrope at a composition of $x_2 = 0.64$.

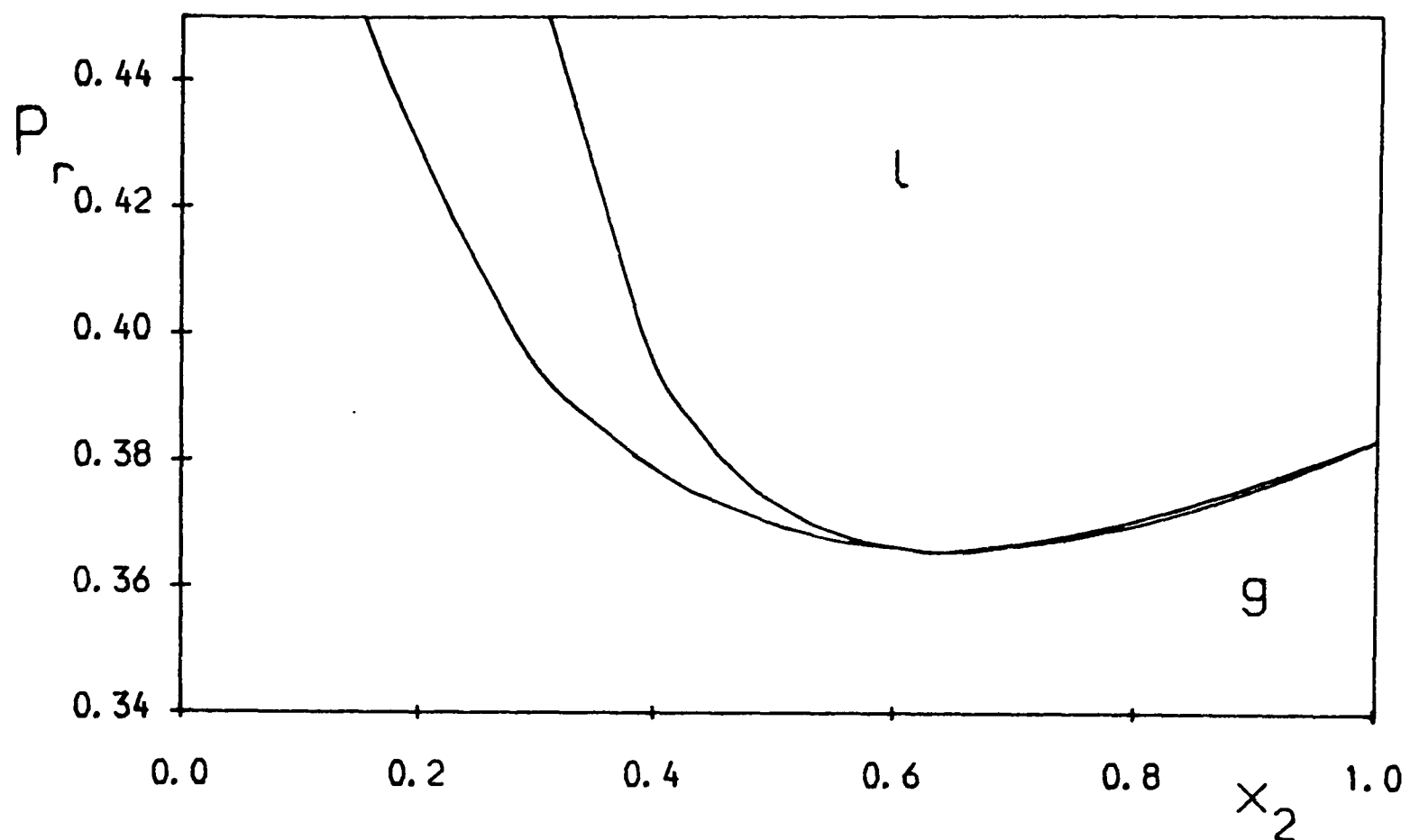


Fig. 6.6 The Px phase diagram for the configurational van der Waals equation at a reduced temperature of $T_r = 0.8000$.

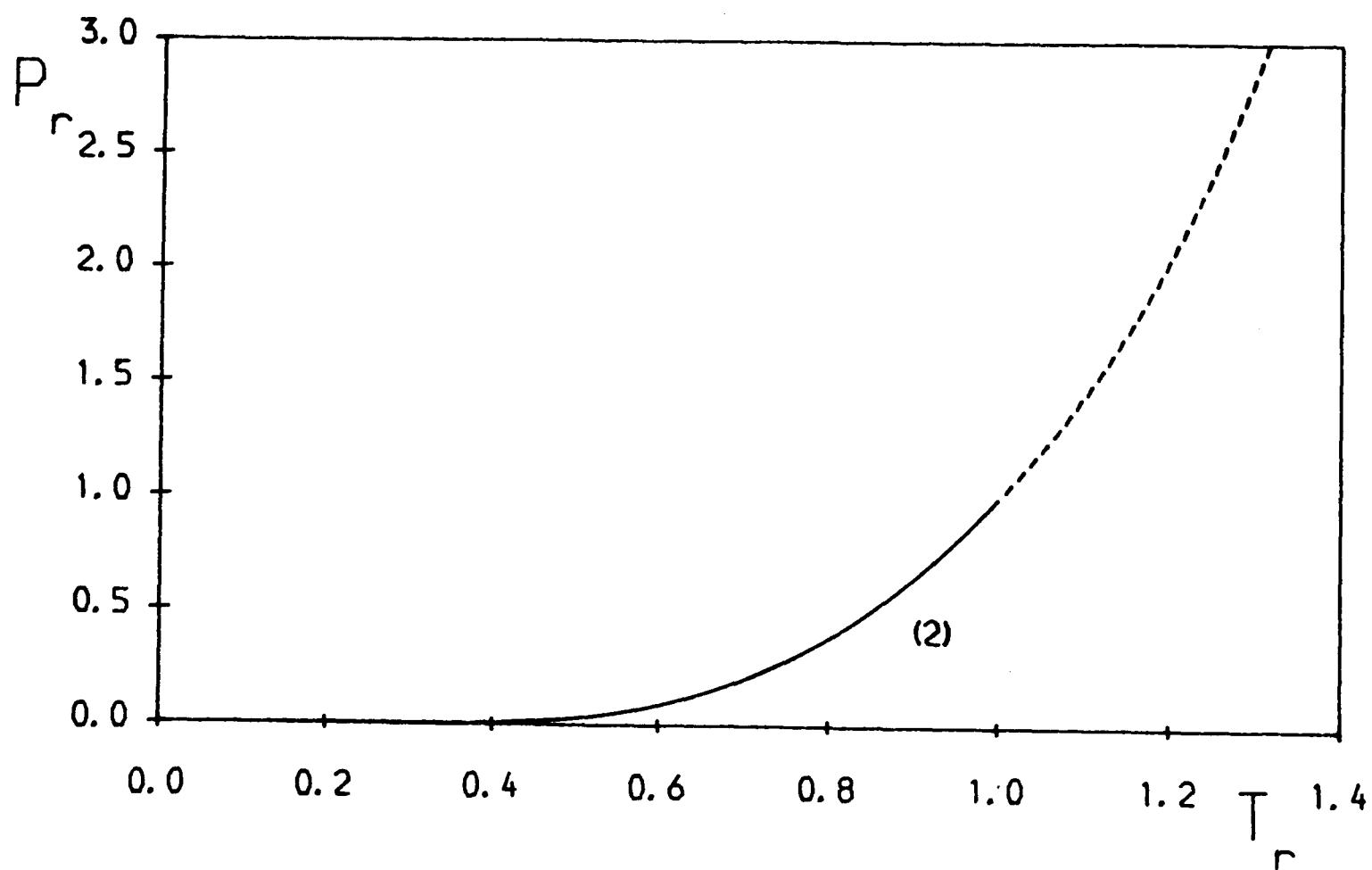


Fig. 6.7 The pressure-temperature projection.

The pressure-temperature projection of the PTx surface is depicted in Fig. 6.7. The solid curve 2 represents the vapour pressure curve for the pure van der Waals fluid, and the dashed curve represents the gas-liquid critical line. The azeotropic line is not shown.

6.3 CONCLUSION

The results obtained in Section 6.1.2 for binary mixtures of points (1) and van der Waals molecules (2) with $a_{11}=0$ and $a_{12}=a_{22}/2$ are very similar to those of the equivalent mixture of points and hard cores (Section 4.8.2). Both systems show gas-liquid and liquid-liquid phase coexistence; the van der Waals mixture's phase diagrams are more complicated due to the greater extent of liquid-liquid immiscibility. Hence, the presence of liquid-liquid phase equilibria in the mixtures of points and hard cores of Chapter 4 does not seem to be an artefact of the hard sphere equations.

The van der Waals equation derived from the configurational integral does not predict liquid-liquid coexistence for a binary mixture of point particles and van der Waals molecules. This is in contrast with the results obtained from the other van der Waals equation as well as with those obtained using the Mansoori equation (Section 4.8.2). The reason for this behaviour seems to be due to the different ranges of reduced densities that each equation calculates.

The Mansoori et al. equation has a pole at a reduced density of $\eta=1.0$, and consequently densities in the range of $\eta=0$ to 1 are possible. The ordinary van der Waals equation for a mixture of points (1) and van der Waals molecules (2) has a pole which varies with composition $1/(1+3x_2)$; at a composition of $x_2=1$ the pole is a reduced density of $\eta=0.25$, and at a composition of $x_2=0$ the pole is $\eta=1$. Hence, this equation also enables reduced densities in the range of $\eta=0$ to 1. However, the van der Waals equation obtained from the configurational integral has a fixed pole of $\eta=0.25$ as for the pure van der Waals fluid with a density range of $\eta=0$ to 0.25. Because densities above $\eta=0.25$ are not calculated by this equation, important liquid roots in the range $\eta=0.25$ to 0.5 will not be represented. This is probably why the equation derived from the configurational integral does not show the liquid-liquid coexistence predicted by the other two equations. The fact that the van der Waals configurational equation cannot calculate portions of the phase diagram is consistent with the shifting of the azeotrope to much higher mole fractions.

CHAPTER 7

LATTICE MIXTURES

In this chapter Robledo's exact thermodynamic correspondence between lattice mixtures and simpler magnetic spin systems [61] is used to calculate the coexistence curves for mixtures of AA and ab bifunctional molecules. If the AA molecule represents water and the asymmetric ab molecule represents surfactant, then the model mixture's phase equilibria can be compared with the phase diagrams obtained experimentally for aqueous surfactant solutions. Although this model system oversimplifies some features of the real mixtures, it provides invaluable information about the mechanisms of phase separation in amphiphile-water systems.

Thermodynamic interconnections between the theories of ferromagnetism, antiferromagnetism, the "lattice gas", the order-disorder transition in alloys, and binary liquid solutions are well established [62],[63]. The problems these systems pose in statistical mechanics can all be related, with varying degrees of approximation, to a simple statistical model often referred to as the "Ising Model" [64]. Since the most important developments in this

field have been presented in papers using the language of ferromagnetism, magnetic systems are discussed first in Section 7.1. The thermodynamic correspondence between the spin systems and binary lattice mixtures is discussed in Section 7.2.

7.1 MAGNETIC SYSTEMS

7.1.1 The Equation Of State

The simplest magnetic system is the spin-1/2 where there are two allowed spin orientations -1 or +1 at each site of a lattice. A route to an equation of state for a spin-1/2 Ising model is possible by using the Bragg-Williams approximation [65]. The resulting mean-field equation can be written

$$\frac{H}{kT'} = \ln \left(\frac{1+m}{1-m} \right) - \frac{zmJ}{kT'}$$

where H denotes the magnetic field, m the magnetization, and J is the coupling constant between spins. The temperature of the Ising magnet is T' , and z is the coordination number of the lattice. This equation can be used to locate the Curie point or critical point of a ferromagnetic crystal at which the spontaneous magnetization, and hence the difference between two differently oriented magnetic domains, goes to zero as the temperature is increased.

7.1.2 The Critical Point

The spin system's critical point can be determined by using the following conditions:

$$H = 0, \quad \left(\frac{\partial H}{\partial m} \right)_{T'} = 0, \quad \left(\frac{\partial^2 H}{\partial m^2} \right)_{T'} = 0$$

$$\frac{1}{kT'} \left(\frac{\partial H}{\partial m} \right)_{T'} = \frac{1}{1+m} + \frac{1}{1-m} - \frac{zJ}{kT'} = 0$$

$$\frac{1}{kT'} \left(\frac{\partial^2 H}{\partial m^2} \right)_{T'} = \frac{-1}{(1+m)^2} + \frac{1}{(1-m)^2} = 0$$

By solving these two mean-field equations simultaneously, values for the critical magnetization and temperature are obtained for the Curie point of the spin-1/2 magnet.

$$m_c = 0, \quad kT'_c = zJ/2$$

The parameter ξ_{13}^c is defined as

$$\xi_{13}^c = \exp(-2J/kT'_c) = \exp(-4/z)$$

For a simple cubic lattice with $z=6$ this function takes the value $\xi_{13}^c=0.51342$. This is the mean-field result for the spin-1/2 Ising magnet. However, the exact solution of Onsager for a two dimensional spin-1/2 Ising model with nearest-neighbour interactions is $\xi_{13}^c=0.64183$ [63]. This result would correspond to a value of the coordination number of $z=9.0206$ in the mean-field case. Consequently, these two values of $\xi_{13}^c=0.51342$ and 0.64183 have been used

to calculate the critical points of the corresponding lattice mixtures in Sections 7.2.5-7.2.12.

7.1.3 The Coexistence Curve

Ferromagnets are characterized by the existence of spontaneous magnetization below the Curie value of ξ_3^C . As the magnetic field H passes through zero, the equilibrium magnetization m will change discontinuously with two magnetic phases of magnetization $-m$ and $+m$ in coexistence. The coexistence curve for a spin-1/2 Ising magnet can also be determined by using the Bragg-Williams approximation [65]. The relationship between the magnetization m and the temperature T' can be expressed in terms of the following mean-field expression:

$$\frac{1}{2} \ln \left(\frac{1+m}{1-m} \right) = \tanh^{-1} m = \frac{zmJ}{2kT'},$$

When the temperature is scaled with respect to the Curie temperature, the equation for the coexistence curve written in terms of $t' = T'/T'_C$ becomes

$$\tanh^{-1} m = m/t'$$

or

$$t' = m/\tanh^{-1} m$$

From this expression values of the reduced temperature along the coexistence curve can be obtained for given values of the magnetization. At the Curie point a magnetization of $m=0$ corresponds to a temperature of $t'=1$, and when $m=1$ the temperature takes the value $t'=0$.

$$\lim_{m \rightarrow 0} t' = 2 \left(\frac{1}{1+m} + \frac{1}{1-m} \right)^{-1} = 1, \quad \lim_{m \rightarrow 1} t' = 0$$

Between the reduced temperatures of zero and one, two magnetic phases coexist with magnetizations $-m$ and $+m$. The magnetization remains practically unchanged up to a temperature of approximately $t'=0.3$; it then starts dropping off to zero, slowly at first and finally very rapidly.

7.2 LATTICE AA-ab MIXTURES

The approach of Robledo [61] is a generalization of the Wheeler-Widom [66],[67] lattice mixture of bifunctional molecules AA, BB and AB, where AB acts as an amphiphile that increases the mutual solubility of AA and BB. In the Wheeler-Widom model each molecule is confined to one bond of a regular lattice with the added requirement that only the A or B ends of the molecules meet at a common lattice site. Hence, the A end of one molecule and the B end of another repel infinitely strongly. This model is equivalent to the Ising model in the same lattice with a spin of -1 or $+1$ at each lattice site, and also to the one-component lattice gas with each site occupied or unoccupied.

Robledo investigated the situation which occurs when non-zero interactions are allowed. Consequently, the development of surfactant-like features in the system's phase diagrams can be followed, from those of conventional mixtures, as the amphiphilic character of the ab molecule is gradually increased. The Robledo model describes a three-component lattice mixture of AA, BB, and ab bifunctional molecules. The thermodynamic properties of a binary mixture of AA and ab components can be obtained by setting the number of molecules and the activity of species BB equal to zero. In this case there are six different kinds of end-to-end encounters between the pairs of AA and ab molecules placed on the bonds of a primary lattice. The values of the associated interaction energies are denoted by ϵ_{AA} , ϵ_{aa} , ϵ_{ab} , ϵ_{bb} , ϵ_{Aa} and ϵ_{Ab} ($\epsilon < 0$ for attractions). The lattice is decorated by introducing a secondary and tertiary lattice. q is defined as the coordination number of a secondary lattice which consists of the midpoints of the bonds in the primary lattice. A tertiary lattice with the midpoints of the bonds connecting nearest-neighbour secondary sites is formed by repeating the above procedure. The ends of molecules only interact if they occupy nearest-neighbour secondary sites, and hence the number of tertiary sites represents the total number of pair interactions between the molecules. In Robledo's notation the total number of tertiary sites N_{13} placed between AA and ab molecules represents the number of AA-ab interactions.

The grand partition function for a mixture of N_{AA} AA molecules and N_{ab} ab molecules ($N=N_{AA}+N_{ab}$) is given by

$$\Xi = Q_{33}^{qN/2} \sum \Omega(N_{AA}, N_{ab}) \xi_{13}^{N_{13}} \lambda_1^{N_{AA}}$$

where Robledo's parameters are defined as

$$Q_{33} = \exp(-e_{aa}/kT) + 2\exp(-e_{ab}/kT) + \exp(-e_{bb}/kT)$$

$$\xi_{13} = \exp(-2J_2/kT') = \exp(-\Delta_{aa}/kT) [1 + \exp(-\delta_{13}/kT)] / D_{13}^{1/2}$$

$$\lambda_1 = \exp(-2H/kT') = [4\exp(-d_{aa}/kT) / D_{13}]^{q/2} \zeta_{AA}$$

$$\zeta_{AA} = Z_{AA}/Z_{ab} = \exp[(\mu_{AA} - \mu_{ab})/kT]$$

and

$$D_{13} = 1 + \exp(-d_{ab}/kT) + 2\exp(-(\Delta_{ab} + d_{ab}/2)/kT)$$

$$\Delta_{aa} = e_{aa} - (e_{aa} + e_{AA})/2$$

$$d_{aa} = e_{AA} - e_{aa}$$

$$d_{ab} = e_{bb} - e_{aa}$$

$$\Delta_{ab} = e_{ab} - (e_{aa} + e_{bb})/2$$

$$\delta_{13} = e_{Ab} - e_{Aa}$$

The expression for the grand partition function except for the proportionality constant also represents the partition function of a spin-1/2 Ising model with coupling constant $J=J_2$ and magnetic field $H=-kT'\ln(\lambda_1)/2$ as shown below

$$Z = \lambda_1^{-N/2} \xi_{13}^{-qN/4} \sum \Omega \xi_{13}^{N_{13}} \lambda_1^{N_{AA}}$$

where $\xi_{13}=\exp(-2J_2/kT')$ and $\lambda_1=\exp(-2H/kT')$.

This correspondence between the spin-1/2 model and the AA-ab mixture is difficult to grasp at first, and it can be more easily understood by noting that there are only two possibilities for the occupancy of a given secondary site: the site is occupied by either a molecule of type AA or of type ab.

When the value of ξ_{13} falls below a critical value (e.g. $\xi_{13}^c = 0.64183$ for the simple cubic lattice), there is a discontinuity in the magnetization of the Ising magnet as H passes through zero with $\lambda_1 = 1$. This is characterized by the occurrence of phase separation between isotropic phases in the equivalent AA-ab lattice mixture. The thermodynamic correspondences between the composition x_{AA} of the AA molecules in the mixture and the magnetization m of the spin system, and between the temperature T of the mixture and T' of the magnet are established in the following sections.

7.2.1 Correspondence Between Magnetization And Composition

For the AA-ab lattice mixture the grand partition function can be written

$$\begin{aligned} \Xi &= Q_{33}^{qN/2} \sum_{\Omega} \xi_{13}^{N_{13}} \lambda_1^{N_M} \\ &= \sum_{N_M=0} \Omega \exp(-E/kT) \zeta_{AA}^{N_M} \end{aligned}$$

The mean number $\langle N_{AA} \rangle$ of the AA species is given by

$$\begin{aligned} \langle N_{AA} \rangle &= \frac{\partial \ln \Xi}{\partial \ln \zeta_{AA}} = \frac{\zeta_{AA}}{\Xi} \frac{\partial \Xi}{\partial \zeta_{AA}} \\ &= \frac{\zeta_{AA}}{\Xi} \sum_{N_{AA}=1} N_{AA} \zeta_{AA}^{N_{AA}-1} \Omega \exp(-E/kT) \end{aligned}$$

where the composition is $x_{AA} = \langle N_{AA} \rangle / N$.

In the case of the spin-1/2 Ising system the total magnetization M is also obtained from the partition function in the following way:

$$\begin{aligned} Z &= \lambda_1^{-N/2} \xi_{13}^{-qN/4} \sum \Omega \xi_{13}^{N_{13}} \lambda_1^{N_{AA}} \\ M &= kT' \frac{\partial \ln Z}{\partial H} = kT' \frac{\partial \ln Z}{\partial \ln \lambda_1} \frac{\partial \ln \lambda_1}{\partial H} \\ M &= -2 \frac{\partial \ln Z}{\partial \ln \lambda_1} = -2 \left(-N/2 + \sum_{N_{AA}=1} N_{AA} \Omega \xi_{13}^{N_{13}} \lambda_1^{N_{AA}-1} / \sum_{N_{AA}=0} \Omega \xi_{13}^{N_{13}} \lambda_1^{N_{AA}} \right) \end{aligned}$$

and the magnetization $m = M/N$.

The relationship between M for the Ising model and $\langle N_{AA} \rangle$ for the mixture can be seen by noticing that

$$Q_{33}^{-qN/2} \Xi = \sum_{N_{AA}=0} \Omega \xi_{13}^{N_{13}} \lambda_1^{N_{AA}}$$

and

$$Q_{33}^{-qN/2} \frac{\partial \Xi}{\partial \lambda_1} = \sum_{N_{AA}=1} N_{AA} \Omega \xi_{13}^{N_{13}} \lambda_1^{N_{AA}-1}$$

so that

$$M = -2 \left(-N/2 + \frac{1}{\Xi} \frac{\partial \Xi}{\partial \lambda_1} \right) = N - \frac{2}{\Xi} \frac{\partial \Xi}{\partial \zeta_{AA}} \frac{\partial \zeta_{AA}}{\partial \lambda_1}$$

We also have

$$\frac{\langle N_{AA} \rangle}{Z_{AA}} = \frac{1}{Z} \frac{\partial Z}{\partial \lambda_{AA}}$$

and

$$\frac{\partial Z_{AA}}{\partial \lambda_1} = [4 \exp(-d_{Aa}/kT) / D_{13}]^{-q/2}$$

therefore

$$M/N = 1 - 2 \langle N_{AA} \rangle [4 \exp(-d_{Aa}/kT) / D_{13}]^{-q/2} / (N Z_{AA})$$

$$m = 1 - 2x_{AA} [4 \exp(-d_{Aa}/kT) / D_{13}]^{-q/2} / Z_{AA}$$

At coexistence $H=0$ and $\lambda_1 = \exp(-2H/kT')=1$ with

$$\lambda_1 = Z_{AA} [4 \exp(-d_{Aa}/kT) / D_{13}]^{q/2} = 1, \quad Z_{AA} = [4 \exp(-d_{Aa}/kT) / D_{13}]^{-q/2}$$

so that the following simple correspondence between the magnetization m of the spin-1/2 Ising magnet and the composition x_{AA} of the mixture is obtained:

$$m = 1 - 2x_{AA}$$

The same type of thermodynamic correspondence is seen between the lattice gas and the spin systems.

7.2.2 Correspondence Between The Temperatures

A connection between the temperature T' of the Ising model and the temperature T of the AA-ab mixture can be obtained directly through the definition of ξ_{13} .

$$\xi_{13} = \exp(-2J_2/kT') = \exp(-\Delta_{aa}/kT) [1 + \exp(-\delta_{13}/kT)] / D_{13}^{1/2}$$

When the temperature T' is scaled with respect to the value at the critical point ($t' = T'/T'_c$), and T is reduced with respect to the energy of the A-A interaction $-\epsilon_{AA}$ ($t = kT/-\epsilon_{AA}$), the expression for ξ_{13} becomes

$$\left(\xi_{13}^c \right)^{1/t'} = \exp(-\Delta_{aa}/t) [1 + \exp(-\delta_{13}/t)] / D_{13}^{1/2}$$

with

$$D_{13} = 1 + \exp(-d_{ab}/t) + 2\exp(-(\Delta_{ab} + d_{ab}/2)/t)$$

Note that all the interaction energy parameters Δ_{aa} , δ_{13} , d_{ab} and Δ_{ab} have also been reduced with respect to the energy $-\epsilon_{AA}$. By solving this equation at a given value of the magnet's reduced temperature t' , we can obtain a corresponding value of the temperature t for the AA-ab mixture.

7.2.3 The Critical Points

The critical points for the lattice mixtures of AA and ab molecules can be obtained from the corresponding critical points of the spin system (Section 7.1.2). At the Curie point the magnetization drops to zero, $m=0$. By using the correspondence between m and the composition x_{AA} established in Section 7.2.1, the mixture's critical composition is found to be $x_{AA}=1/2$. This is true for all AA-ab mixtures due to the symmetric nature of the relationship between x_{AA} and m for the spin-1/2 Ising model.

The equation of Section 7.2.2 for the magnet's critical temperature $t'=1$ at a given value of ξ_{13}^C (the mean field result is $\xi_{13}^C=0.51342$ and the exact value is $\xi_{13}^C=0.64183$), is solved numerically for the critical temperature, $t_C=kT_C/-\epsilon_{AA}$, of the AA-ab mixture. Typically, one root for t_C is obtained representing the upper critical point of a coexistence curve. However, for certain values of the attractive interactions, there may be more than one value of t_C that satisfies the equation. It will become clear later that when the function ξ_{13} versus $t^{-1}=-\epsilon_{AA}/kT$ is parabolic in shape and has a minimum in ξ_{13} , two values of the critical temperature t_C may be found for a given value of the magnet's ξ_{13}^C . This behaviour suggests the occurrence of closed-loop coexistence curves, with the larger value of t_C representing the upper critical point and the smaller root representing the lower critical point. In certain cases the ξ_{13} versus t^{-1} plot can acquire a cubic character, and three

values of t_c may be possible for a given value of ξ_{13} . These correspond to an upper and lower critical point representing a closed-loop coexistence curve, and to another upper critical point for an upper consolute curve appearing at lower temperatures.

7.2.4 The Coexistence Curves

The AA-ab mixture's coexistence curve can be obtained from the mean-field expression introduced in Section 7.1.3 for the coexistence curve of the spin-1/2 Ising model.

$$t' = m / \tanh^{-1} m$$

This equation essentially determines the reduced temperature t' at a given value of the magnetization m . The procedure employed to determine the lattice mixture's coexistence curve is the following: first the magnetization m and the temperature t' at which phase separation occurs are determined for the temperature range $0 < t' < 1$. These values of the coexistence magnetizations $-m$ and $+m$, and temperature t' are then used to obtain the corresponding values of the composition x_{AA} and the temperature t for the mixture. The correspondences between m and x_{AA} , and between t' and t established in Sections 7.2.1 and 7.2.2 respectively are restated below.

$$m = 1 - 2x_{AA}, \quad \left(\xi_{13}^c \right)^{1/t'} = \exp(-\Delta_{Ab}/t) [1 + \exp(-\delta_{13}/t)] / D_{13}^{1/2}$$

By varying the value of the magnet's temperature from $t'=1$ at the critical point to values $0 < t' < 1$, the complete x_{AA} versus $t=kT/-\epsilon_{AA}$ coexistence curve for the AA-ab mixture is determined. It is clear that the coexistence curves will be symmetric with critical points at $x_{AA}=1/2$ and t_c corresponding to $m=0$ and $t'=1$.

The AA-ab mixtures are characterized by the five parameters Δ_{Aa} , d_{Aa} , d_{ab} , Δ_{ab} and δ_{13} which are the appropriate functions of the molecular interactions. In the following sections of this chapter the temperature of the lattice mixture T and the interaction parameters Δ_{Aa} , d_{Aa} , d_{ab} , Δ_{ab} and δ_{13} are all reduced with respect to the energy $-\epsilon_{AA}$ of the A-A interaction ($t=kT/-\epsilon_{AA}$ and $\Delta_{Aa}=\Delta_{Aa}/-\epsilon_{AA}$, $d_{Aa}=d_{Aa}/-\epsilon_{AA}$, etc.). The magnitude of Δ_{Aa} controls the mutual solubility of the AA and ab molecules with large positive values indicating immiscibility. δ_{13} is used to make the A-a and A-b interactions asymmetric, making the ab molecule amphiphilic in nature. The main types of phase behaviour obtained for different values of the interactions are now discussed.

7.2.5 Varying Δ_{Aa}

The effect of varying the attractive interaction parameter $\Delta_{Aa} = (\epsilon_{Aa} - (\epsilon_{AA} + \epsilon_{aa})/2) / -\epsilon_{AA}$ for a binary lattice mixture of AA and ab bifunctional molecules is determined in this section. All the other interaction parameters are set to zero, i.e. $\delta_{13} = d_{ab} = \Delta_{ab} = d_{Aa} = 0$. This mixture's plots of δ_{13} against $t^{-1} = -\epsilon_{AA}/kT$ are shown in Fig. 7.1. ξ_{13} decreases monotonically as t^{-1} is increased for all values of $\Delta_{Aa} > 0$. This is equivalent to the ferromagnetic behaviour of spin systems with spontaneous magnetization occurring below ξ_{13}^c . When $\Delta_{Aa} < 0$, ξ_{13} increases with t^{-1} and there is no phase coexistence.

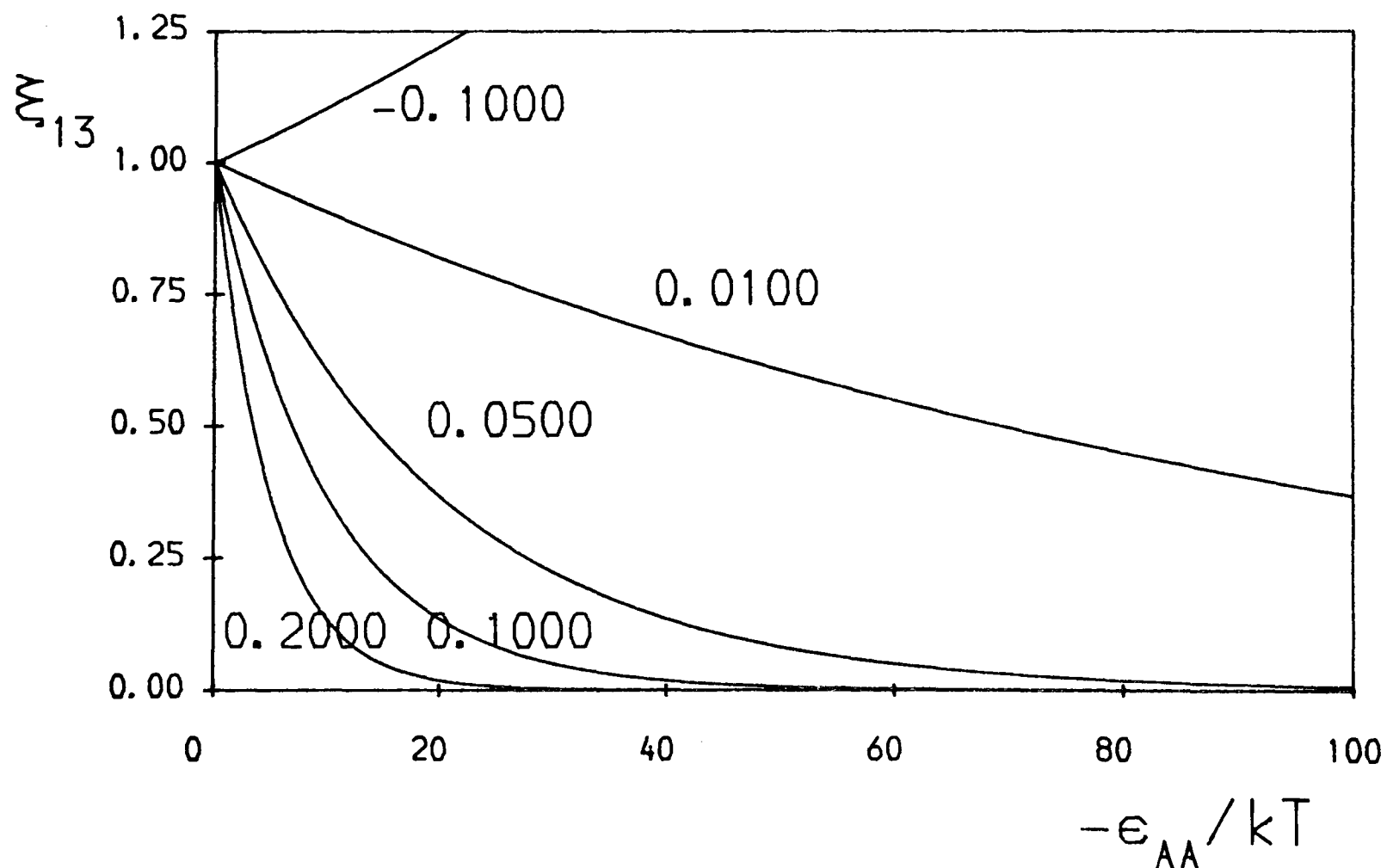


Fig. 7.1 The temperature dependence of ξ_{13} for an AA-ab mixture with $\delta_{13} = d_{ab} = \Delta_{ab} = d_{Aa} = 0$. The values of Δ_{Aa} are labelled on the curves.

The value of the mixture's critical temperature can be obtained for a given critical value of ξ_{13}^c . In this case the correspondence between the spin system's temperature t' and the mixture's temperature t is particularly easy. From the equation of Section 7.2.2 we have

$$\ln(\xi_{13}^c)/t' = -\Delta_{Aa}/t$$

and at the critical point

$$t_c = kT_c/(-e_{AA}) = -\Delta_{Aa}/\ln(\xi_{13}^c)$$

It is now clear that the miscibility of the pure AA and ab fluids is determined by the magnitude of Δ_{Aa} . An increase in Δ_{Aa} will increase the temperature of the critical point, and thus increase the extent of immiscibility. Complete immiscibility is obtained when Δ_{Aa} tends to infinity.

The AA-ab mixture's coexistence curves determined for two values of ξ_{13}^c are shown in Fig. 7.2 and Fig. 7.3. Fig. 7.2 represents the phase behaviour with upper critical points corresponding to the value $\xi_{13}^c=0.51342$. In all cases the compositions of the coexisting phases tend to zero and one as the temperature approaches zero.

The extent of immiscibility between the species AA and ab increases as the value of Δ_{AA} increases, corresponding to strong interactions between like species. This phase behaviour is not unexpected and is seen with many simple systems. In the case of the binary mixtures of equal-sized hard cores investigated in Chapter 5, the extent of liquid-liquid immiscibility increased as the attractive interactions between unlike species was weakened. The same type of behaviour is seen when the critical point corresponds to $\xi_{13}^C = 0.64183$ as shown in Fig. 7.3. When ξ_{13}^C is changed from a value $\xi_{13}^C = 0.51342$ to 0.64183 at a fixed value of Δ_{AA} , the critical temperature increases. It is also interesting to note that all the coexistence curves scale with respect to t/t_C .

In the next section the ab bifunctional molecule of the AA-ab mixture is given a surfactant-like character with an asymmetry in the interaction energies ϵ_{AA} and ϵ_{Ab} . As we shall see the mixture's phase diagrams are more complicated than when $\epsilon_{AA} = \epsilon_{Ab}$.

Δ_{Aa}	Upper Critical Point $kT_C/-\epsilon_{AA}$
0.0100	1.5×10^{-2}
0.0500	7.5×10^{-2}
0.1000	1.5×10^{-1}
0.2000	3.0×10^{-1}

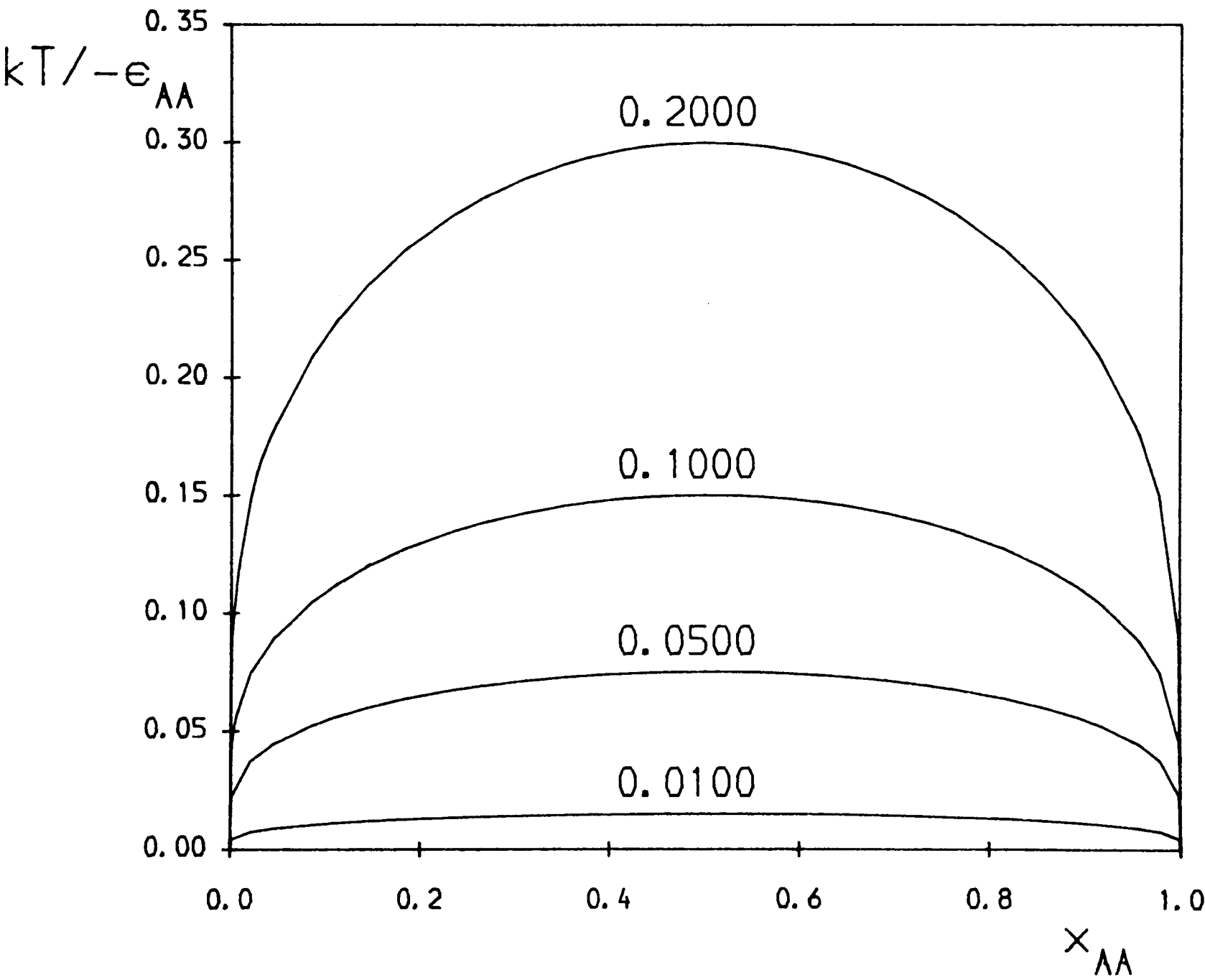


Fig. 7.2 Coexistence curves for an AA-ab mixture with $\delta_{13}=d_{ab}=\Delta_{ab}=d_{Aa}=0$ for $\xi_{13}^C=0.51342$. The values of Δ_{Aa} are labelled on the curves.

Δ_{Aa}	Upper Critical Point $kT_c/-\epsilon_{AA}$
0.0100	2.2551×10^{-2}
0.0500	1.1128×10^{-1}
0.1000	2.2551×10^{-1}
0.2000	4.5103×10^{-1}

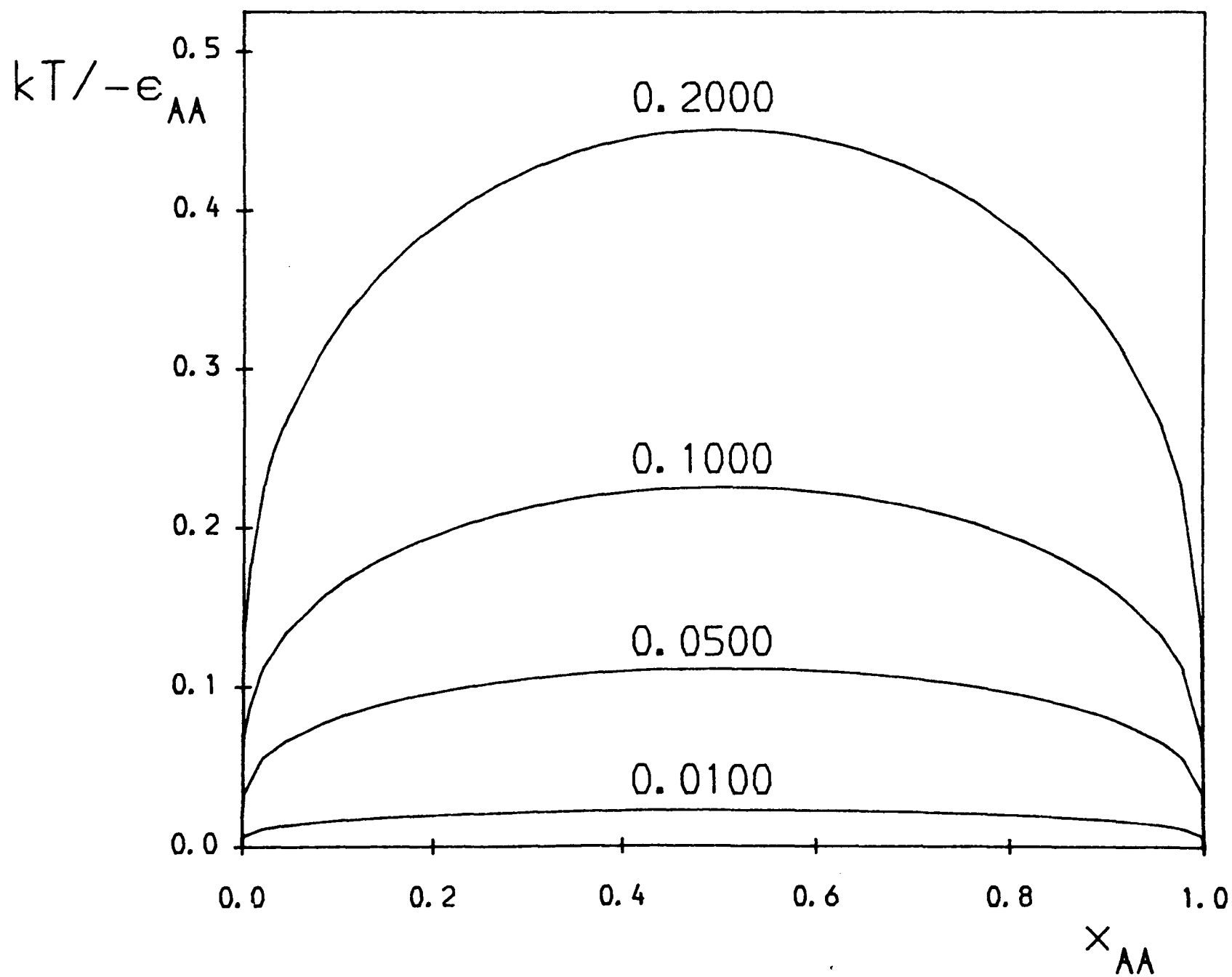


Fig. 7.3 Coexistence curves for an AA-ab mixture with $\delta_{13}=d_{ab}=\Delta_{ab}=d_{Aa}=0$ for $\xi_{13}^c=0.64183$. The values of Δ_{Aa} are labelled on the curves.

7.2.6 Varying δ_{13}

In this case we have an AA-ab mixture with a fixed value of $\Delta_{Aa}=0.1$ and $d_{ab}=\Delta_{ab}=d_{Aa}=0$. The action of ab as an amphiphile can be controlled by varying the attractive forces involved in $\delta_{13}=(\epsilon_{Ab}-\epsilon_{Aa})/-\epsilon_{AA}$. Essentially δ_{13} measures the difference in the interactions of the AA molecule with the two ends of the ab molecule. Fig. 7.4 shows the variation of ξ_{13} with t^{-1} for various values of δ_{13} , labelled on the curves. As the value of δ_{13} is made increasingly negative, the curves acquire a minimum and become parabolic in shape. Two roots for $t_c=-\epsilon_{AA}/kT_c$ are possible for a given value of ξ_{13}^c when $\delta_{13}<-0.1$, indicating closed-loop coexistence.

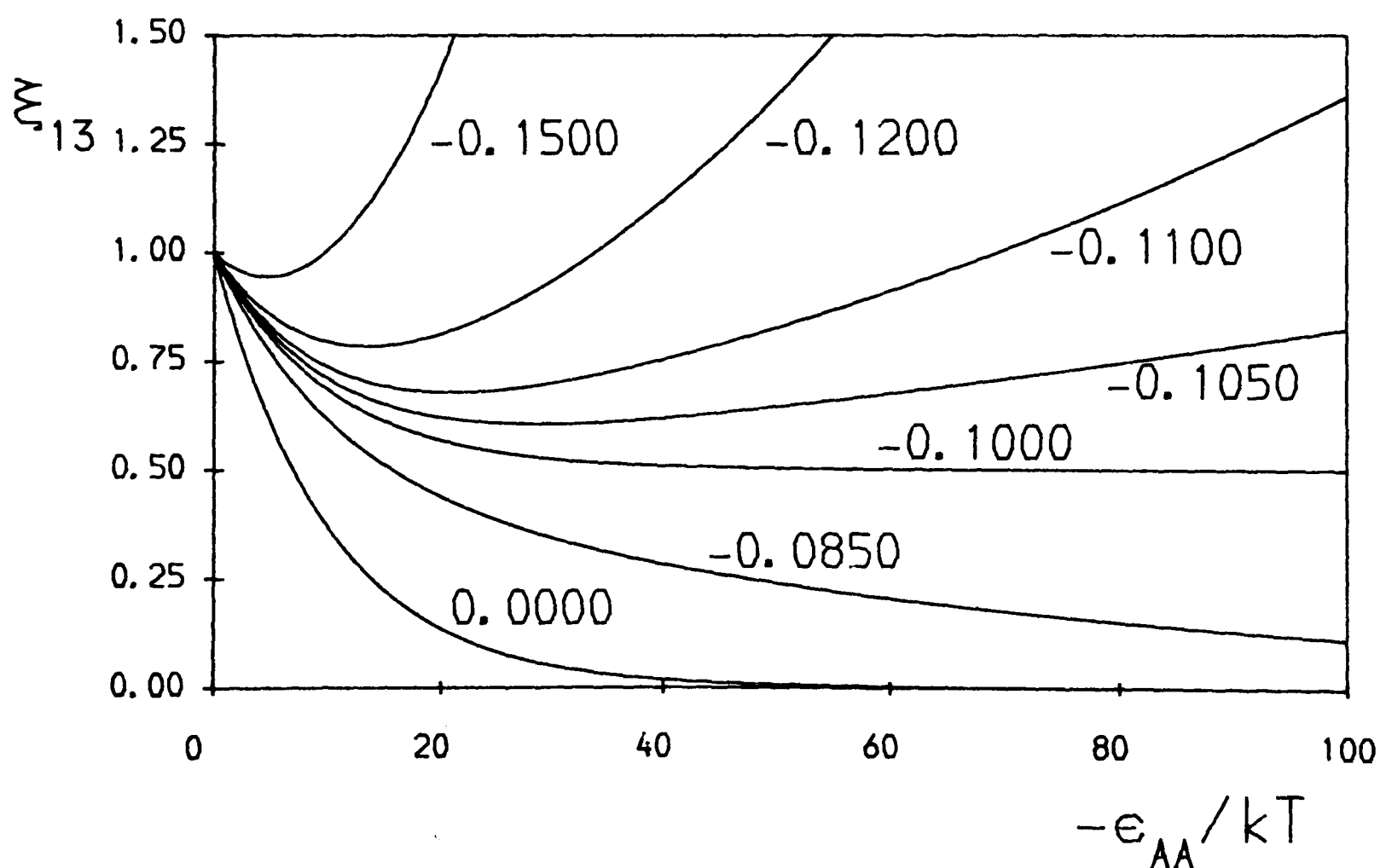


Fig. 7.4 The temperature dependence of ξ_{13} for an AA-ab mixture with $\Delta_{Aa}=0.1$ and $d_{ab}=\Delta_{ab}=d_{Aa}=0$. The values of δ_{13} are labelled on the curves.

The coexistence curves calculated with $\xi_{13}^c=0.51342$ and 0.64183 are shown in Fig. 7.5 and Fig. 7.6 respectively. As expected these phase diagrams show that a decrease in δ_{13} introduces surfactant-like behaviour, and the extent of coexistence is diminished. When $\delta_{13}<-0.1$ closed-loop coexistence curves are seen with corresponding upper and lower critical points. A further increase in the surfactant nature of the ab molecule results in the total disappearance of immiscibility. In these cases there are no values of t_c that satisfy the equation for ξ_{13}^c .

There is a special limiting case when the phase behaviour changes from that of closed-loop coexistence to that of a single upper consolute curve. For this particular mixture the transition occurs when $\Delta_{Aa}=0.1$ and $\delta_{13}=-0.1$. This can be seen in Fig. 7.4 with a limiting value of ξ_{13} as the temperature goes to zero:

$$\xi_{13} = \left(\xi_{13}^c \right)^{1/t'} = \exp(-\Delta_{Aa}/t) [1 + \exp(-\delta_{13}/t)] / D_{13}^{1/2}$$

and therefore

$$\lim_{t \rightarrow 0} \xi_{13} = \left(\xi_{13}^c \right)^{1/t'} = 1/2, \quad t' = \ln(1/2) / \ln(\xi_{13}^c)$$

Hence, we will have limiting values of the coexisting compositions differing from zero and one when the mixture's temperature t tends to zero. These limiting values of x_{AA} can be calculated from the temperature t' corresponding to $\xi_{13}=1/2$ by determining the coexisting magnetizations

$-m$ and $+m$ using the equation of Section 7.1.3. These values of the magnetization are used to calculate the limiting values of the composition with the help of the usual expression $x_{AA}=(1-m)/2$. The zero temperature $t=0$ limits of the coexisting compositions for $\xi_{13}^C=0.51342$ are $x_{AA}=1/3$ and $x_{AA}=2/3$, and for $\xi_{13}^C=0.64183$ they are $x_{AA}=0.060035$ and $x_{AA}=0.93996$. When $\delta_{13}>-0.1$ the upper consolute curve has the usual $t=0$ limits of x_{AA} with values of zero and one, and when $\delta_{13}<0.1$ closed-loops are seen.

The phase diagrams of the AA-ab mixture obtained when the molecules ab are given a surfactant-like character have been investigated by varying the parameter δ_{13} . It appears that closed-loop coexistence curves can be obtained by simply decreasing the value of δ_{13} and creating an asymmetry between the ϵ_{Aa} and ϵ_{Ab} interactions. In the present notation, if the AA species represents the water molecules and the ab species represents the surfactant molecules of an aqueous surfactant solution, then the a end of ab is hydrophobic and the b end is hydrophilic, i.e. $\delta_{13}<0$. Systems with $\delta_{13}>0$ have phase diagrams with the usual upper consolute solution curves, and there is an increase in immiscibility with increasing δ_{13} .

δ_{13}	Upper Critical Point, $kT_C/-\epsilon_{AA}$	Lower Critical Point, $kT_C/-\epsilon_{AA}$
-0.0990	3.4555×10^{-2}	-
-0.1000	2.7639×10^{-2}	-
-0.1001	2.6527×10^{-2}	3.7764×10^{-3}
-0.1003	2.3399×10^{-2}	1.1394×10^{-2}
-0.1004	1.9835×10^{-2}	1.6559×10^{-2}

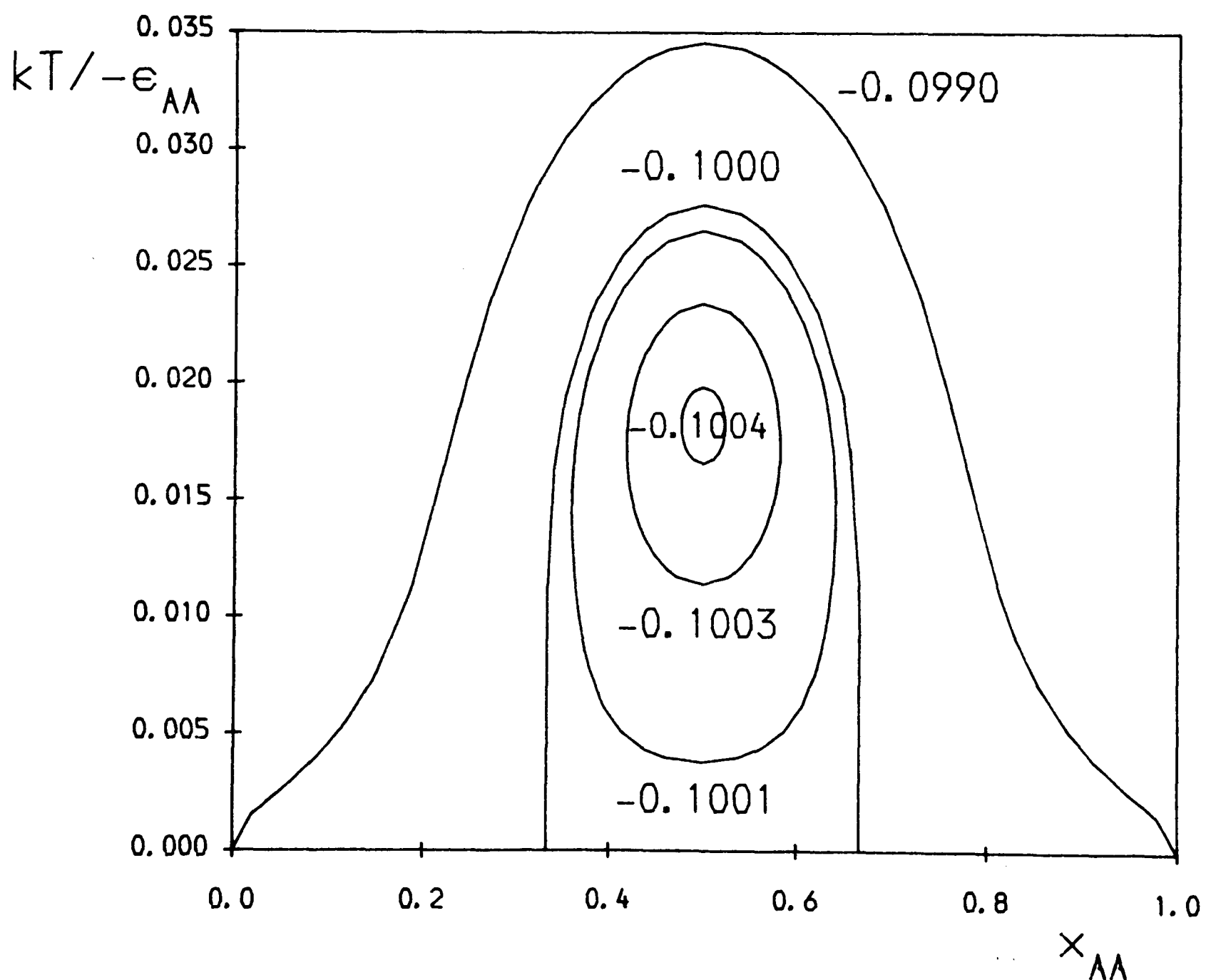


Fig. 7.5 Coexistence curves for an AA-ab mixture with $\Delta_{AA}=0.1$ and $d_{ab}=\Delta_{ab}=d_{AA}=0$ for $\xi_{13}^C=0.51342$. The values of δ_{13} are labelled on the curves.

δ_{13}	Upper Critical Point, $kT_C/-\epsilon_{AA}$	Lower Critical Point, $kT_C/-\epsilon_{AA}$
-0.0950	9.1870×10^{-2}	-
-0.1000	7.9366×10^{-2}	-
-0.1020	7.3398×10^{-2}	8.0092×10^{-3}
-0.1050	6.2097×10^{-2}	2.0513×10^{-2}
-0.1073	4.4183×10^{-2}	3.8092×10^{-2}

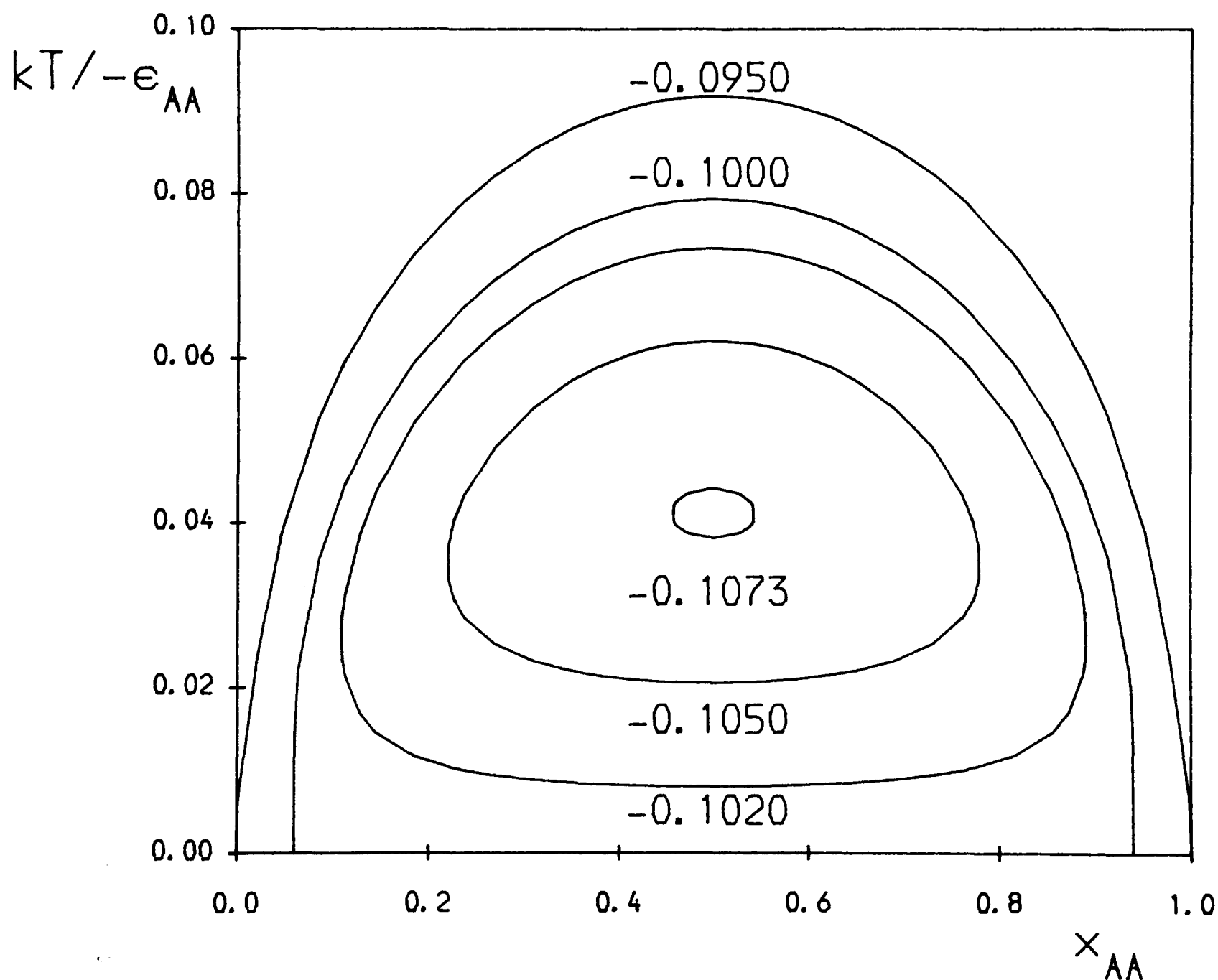


Fig. 7.6 Coexistence curves for an AA-ab mixture with $\Delta_{Aa}=0.1$ and $d_{ab}=\Delta_{ab}=d_{Aa}=0$ for $\xi_{13}^C=0.64183$ The values of δ_{13} are labelled on the curves.

7.2.7 Varying d_{ab}

The effect on the phase behaviour of changing $d_{ab} = (\epsilon_{bb} - \epsilon_{aa}) / -\epsilon_{AA}$ is shown in Fig. 7.7 for mixtures with $\Delta_{AA} = 0.1$, $\delta_{13} = -0.12$, and $\Delta_{ab} = d_{AA} = 0$. When d_{ab} is made increasingly negative, the parabolic curve gradually becomes cubic-like in character, so that there is a possibility of three values of t_c satisfying the equation for ξ_{13}^c . Two of the roots represent the upper and lower critical points of a closed loop, and the third represents the critical point of an upper consolute curve occurring at lower temperatures. If d_{ab} is decreased even further the closed-loop feature disappears altogether, and only an upper consolute curve remains.

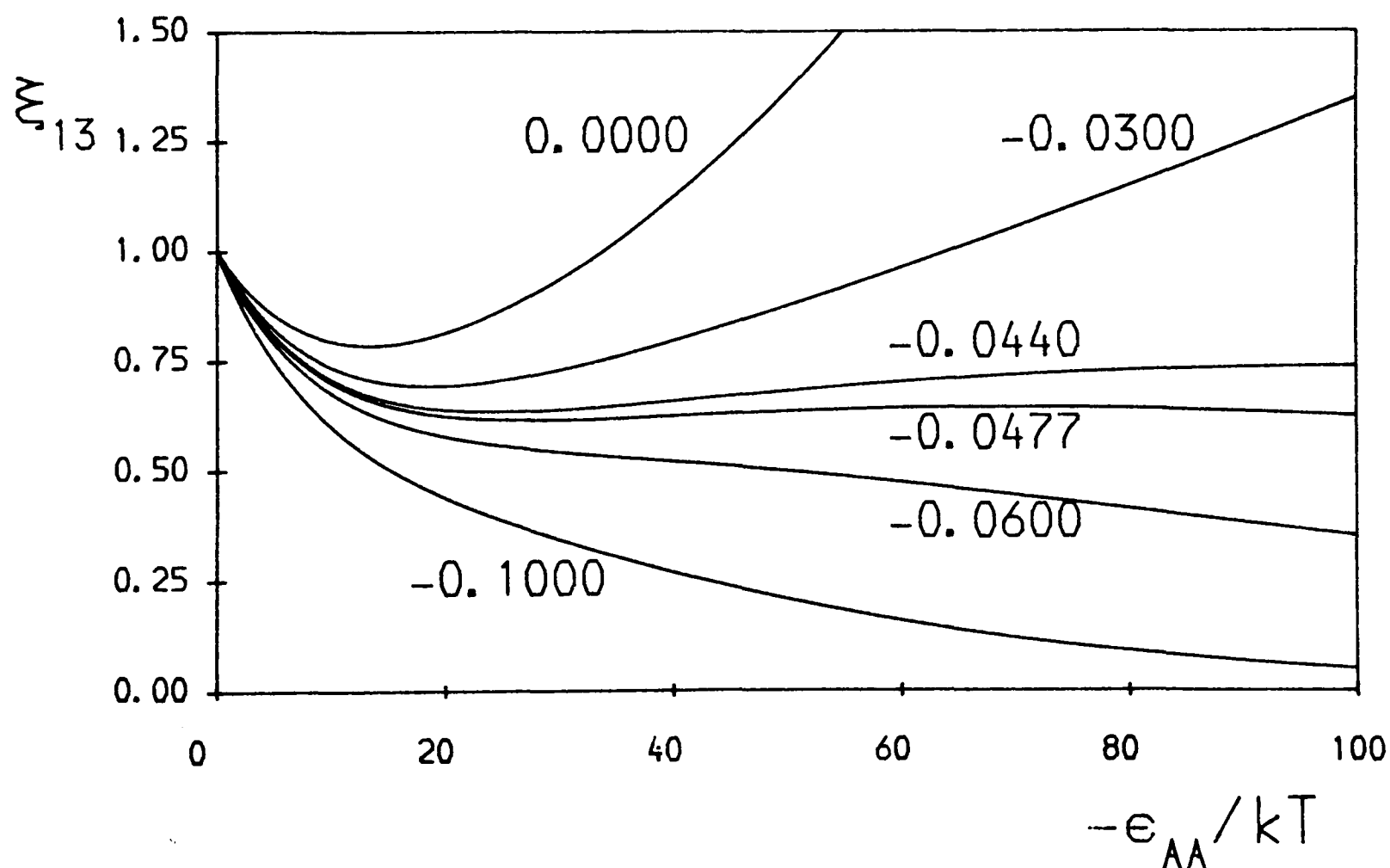


Fig. 7.7 The temperature dependence of ξ_{13} for an AA-ab mixture with $\Delta_{AA} = 0.1$, $\delta_{13} = -0.12$ and $\Delta_{ab} = d_{AA} = 0$. The values of d_{ab} are labelled on the curves.

This will become clearer from an investigation of the phase diagrams. The coexistence curves for the AA-ab mixtures with $\Delta_{Aa}=0.1$, $\delta_{13}=-0.1004$ and $\Delta_{ab}=d_{Aa}=0$ are shown in Fig. 7.8. A progression from a closed-loop to an upper consolute curve can be seen as d_{ab} is decreased for a value of $\xi_{13}^C=0.51342$. No new features are exhibited because the value of ξ_{13}^C is too low. However, when ξ_{13}^C is increased to the exact value of $\xi_{13}^C=0.64183$, a new feature of the phase behaviour emerges as seen in Fig. 7.9 for the mixtures with $\Delta_{Aa}=0.1$, $\delta_{13}=-0.12$ and $\Delta_{ab}=d_{Aa}=0$. As d_{ab} is made increasingly negative an upper consolute solution curve appears at lower temperatures. This curve eventually merges into the closed-loop to give a single coexistence curve which retains some of the characteristics of the closed-loop with thinning in the central region; see a value of $d_{ab}=-0.0479$ in Fig. 7.9. The usual upper consolute curves are obtained when d_{ab} is made sufficiently negative.

It appears that the parameters d_{ab} and δ_{13} have an opposing effect on the phase behaviour. As d_{ab} is made more negative, it competes against δ_{13} with the ϵ_{bb} interactions finally winning over the ϵ_{Ab} interactions. In a sense the attractive interactions between the b ends of the bifunctional ab molecule have counteracted the molecule's surfactant character, since ab prefers to interact with itself than with AA. It must be noted that only small changes in the value of the parameter d_{ab} are required to completely change the type of behaviour that is observed.

d_{ab}	Upper Critical Point, $kT_C/-\epsilon_{AA}$	Lower Critical Point, $kT_C/-\epsilon_{AA}$
0.0000	1.9835×10^{-2}	1.6559×10^{-2}
-0.0005	2.3955×10^{-2}	1.0381×10^{-2}
-0.0010	2.5979×10^{-2}	5.4480×10^{-3}
-0.0050	3.4253×10^{-2}	-

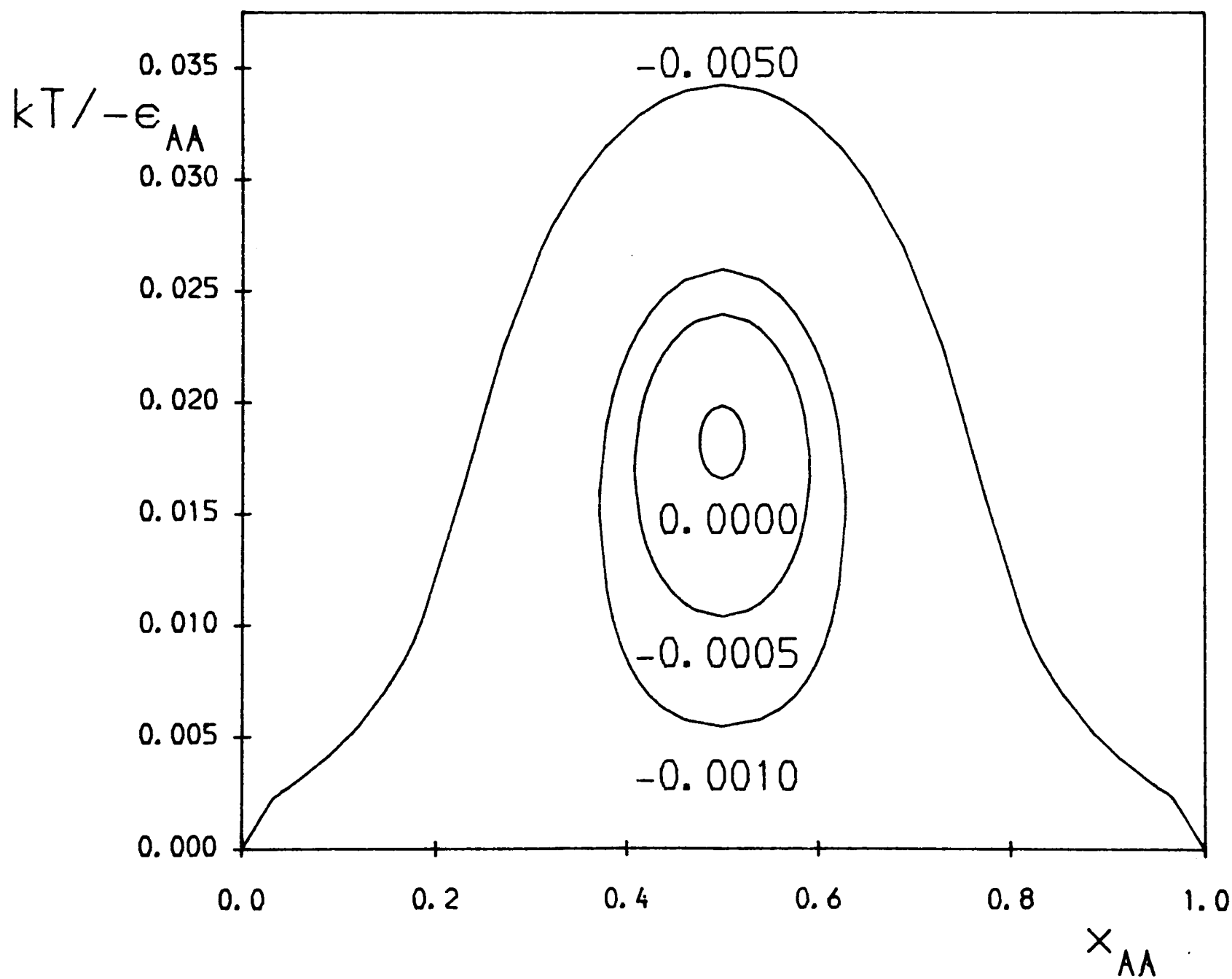


Fig. 7.8 Coexistence curves for an AA-ab mixture with $\Delta_{AA}=0.1$, $\delta_{13}=-0.1004$ and $\Delta_{ab}=d_{AA}=0$ for $\xi_{13}^C=0.51342$. The values of d_{ab} are labelled on the curves.

d_{ab}	Upper Critical Point, $kT_c/-\epsilon_{AA}$	Lower Critical Point, $kT_c/-\epsilon_{AA}$	Upper Critical Point, $kT_c/-\epsilon_{AA}$
-0.0440	5.4447×10^{-2}	3.0849×10^{-2}	4.5964×10^{-3}
-0.0477	6.3237×10^{-2}	1.6122×10^{-2}	1.3248×10^{-2}
-0.0479	6.3617×10^{-2}	-	-
-0.0600	8.1072×10^{-2}	-	-

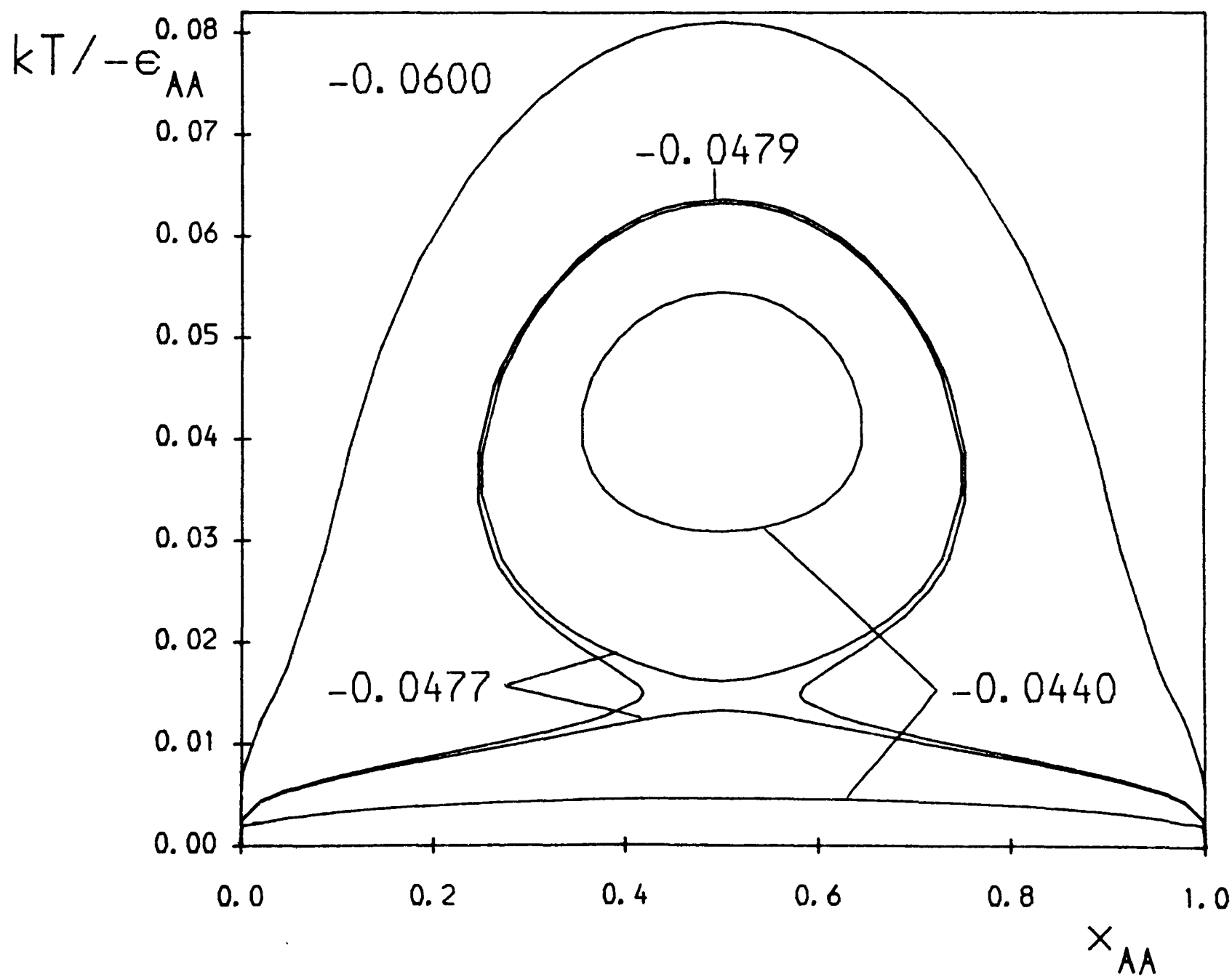


Fig. 7.9 Coexistence curves for an AA-ab mixture with $\Delta_{Aa}=0.1$, $\delta_{13}=-0.12$ and $\Delta_{ab}=d_{Aa}=0$ for $\xi_{13}^c=0.64183$. The values of d_{ab} are labelled on the curves.

7.2.8 Varying Δ_{ab}

The properties of a mixture with $\Delta_{Aa}=0.1$, $\delta_{13}=-0.12$ and $d_{ab}=d_{Aa}=0$ have been investigated for various values of the parameter $\Delta_{ab}=(\epsilon_{ab}-(\epsilon_{aa}+\epsilon_{bb})/2)/-\epsilon_{AA}$. Fig. 7.10 shows the effect that Δ_{ab} has on the ξ_{13} versus reciprocal temperature plot. The behaviour of this system is very similar to that of the previous system which investigated changes in d_{ab} . Δ_{ab} is seen to counteract the surfactant effect of δ_{13} ; the closed-loop coexistence curves obtained when $\Delta_{ab}=0$ become upper consolute curves as Δ_{ab} is made increasingly negative. Again the surfactant-surfactant interactions compete against the surfactant-water interactions.

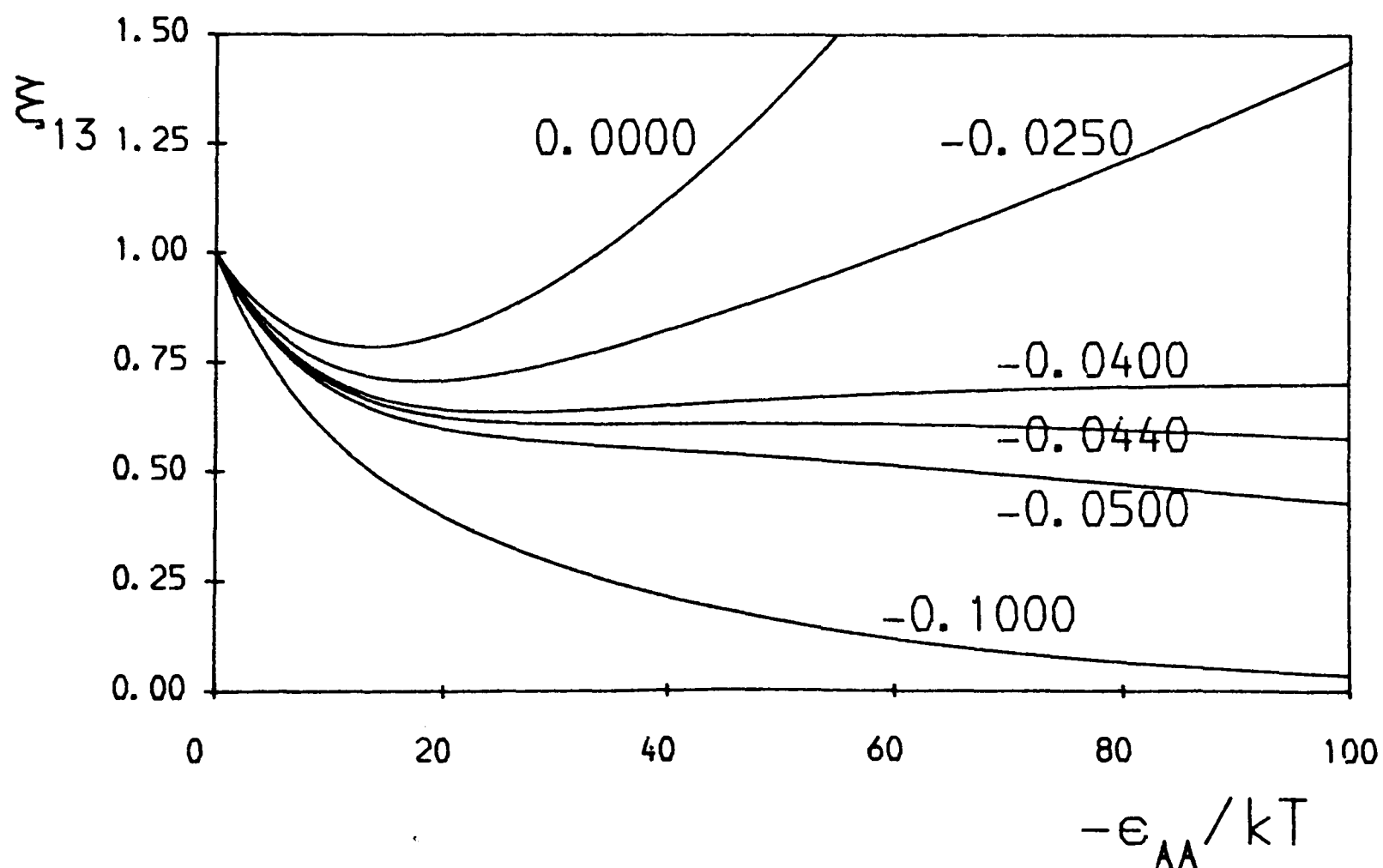


Fig. 7.10 The temperature dependence of ξ_{13} for an AA-ab mixture with $\Delta_{Aa}=0.1$, $\delta_{13}=-0.12$ and $d_{ab}=d_{Aa}=0$. The values of Δ_{ab} are labelled on the curves.

7.2.9 Varying d_{ab} With $\delta_{13}=0$

The study of Section 7.2.7 investigated the effect of d_{ab} on the phase behaviour of mixtures with $\Delta_{Aa}=0.1$, $\delta_{13}=-0.12$, and $\Delta_{ab}=d_{Aa}=0$. This section presents a brief summary of the results obtained when $\delta_{13}=0$. The temperature dependence of ξ_{13} is shown in Fig. 7.11 for different values of d_{ab} . Decreasing d_{ab} , marginally increases the extent of immiscibility between the two coexisting phases. However, this system does not exhibit any new features.

In all the AA-ab mixtures investigated up to now Δ_{Aa} has always been positive, $\Delta_{Aa}>0$. A survey of the results with negative values of Δ_{Aa} , $\Delta_{Aa}<0$, is undertaken in the following sections.

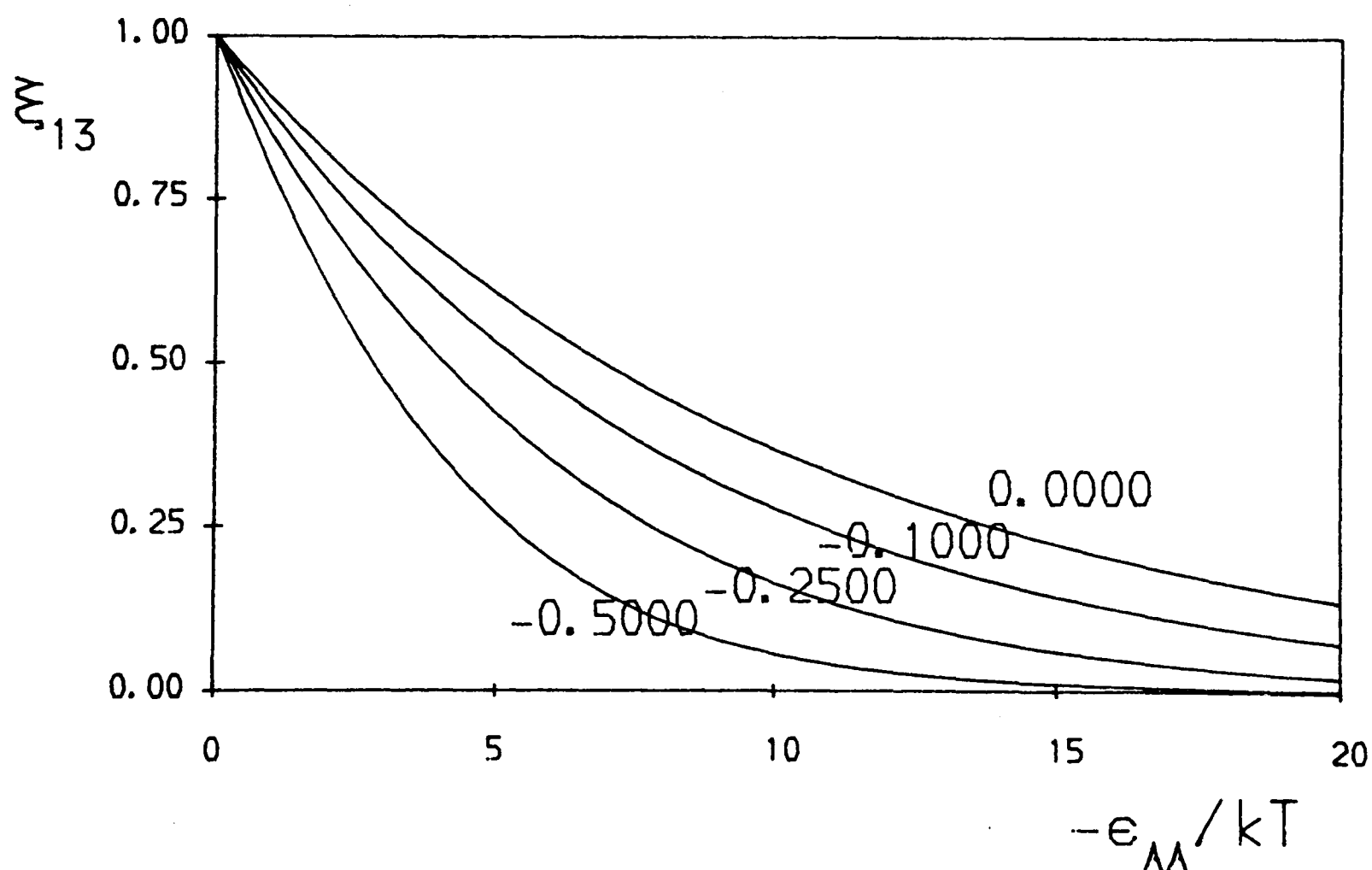


Fig. 7.11 The temperature dependence of ξ_{13} for an AA-ab mixture with $\Delta_{Aa}=0.1$, and $\delta_{13}=\Delta_{ab}=d_{Aa}=0$. The values of d_{ab} are labelled on the curves.

7.2.10 Varying δ_{13} With $\Delta_{Aa}=-0.1$

When $\Delta_{Aa} < 0$ and $\delta_{13} = d_{ab} = \Delta_{ab} = d_{Aa} = 0$, there are no solutions for $t < 1$ which correspond to a value of ξ_{13} . In the case of the spin-1/2 Ising magnet this corresponds to a negative value of the coupling constant $J < 0$ with antiferromagnetism. Consequently, the corresponding AA-ab mixture does not exhibit phase coexistence. However, if δ_{13} is increased sufficiently, roots for $t < 1$ satisfying ξ_{13} become possible (see Fig. 7.12). An increase in δ_{13} enables closed-loop coexistence curves similar to those of Section 7.2.6. Again the strong asymmetry of the ab molecule seems to be the primary cause for the presence of closed-loops.

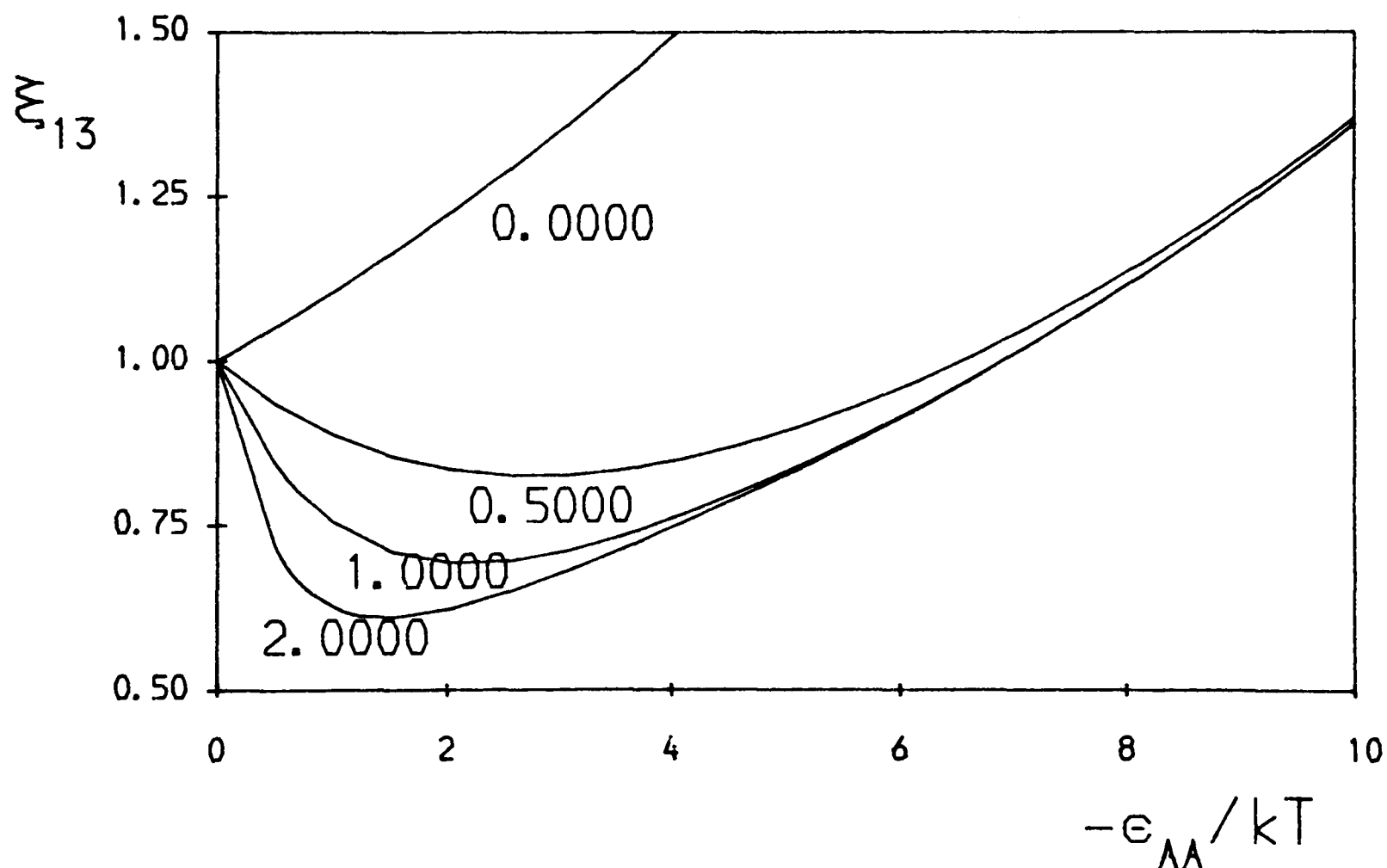


Fig. 7.12 The temperature dependence of ξ_{13} for an AA-ab mixture with $\Delta_{Aa} = -0.1$ and $d_{ab} = \Delta_{ab} = d_{Aa} = 0$. The values of δ_{13} are labelled on the curves.

7.2.11 Varying d_{ab} With $\Delta_{Aa}=-0.1$

The system of interest in this section is an AA-ab mixture with values of the interaction parameters of $\Delta_{Aa}=-0.1$ and $\delta_{13}=\Delta_{ab}=d_{Aa}=0$. The effect that varying the parameter d_{ab} has on the curves of ξ_{13} against $t^{-1}=-\epsilon_{AA}/kT$ is shown in Fig. 7.13. By making d_{ab} more negative when $\Delta_{Aa}=-0.1$, coexistence is made possible, but only one value of t_c is found for a given value of ξ_{13}^c . Hence, the usual upper consolute coexistence curves are obtained when d_{ab} is large and negative. No new types of features emerge with this system.

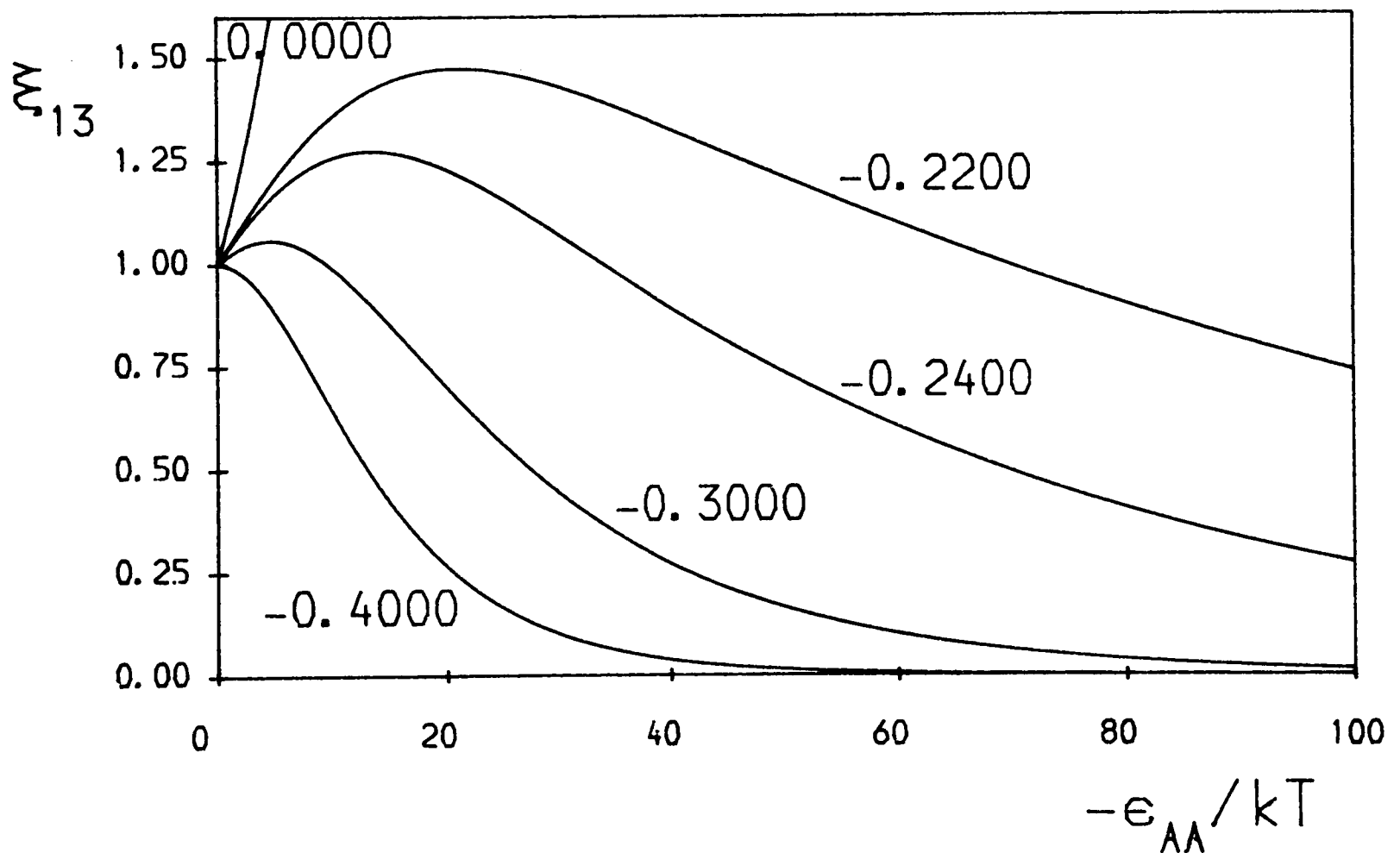


Fig. 7.13 The temperature dependence of ξ_{13} for an AA-ab mixture with $\Delta_{Aa}=-0.1$ and $\delta_{13}=\Delta_{ab}=d_{Aa}=0$. The values of d_{ab} are labelled on the curves.

7.2.12 Varying d_{ab} With $\Delta_{Aa}=-0.1$ And $\delta_{13}=0.5$

The last AA-ab mixtures investigated have values of the interaction parameters of $\Delta_{Aa}=-0.1$, $\delta_{13}=0.5$ and $\Delta_{ab}=d_{Aa}=0$. Fig. 7.14 shows the temperature dependence of ξ_{13} versus t for different values of d_{ab} . For some values of ξ_{13} there are three values of t . The coexistence curves for $\xi_{13}^c=0.64183$ with $\Delta_{Aa}=-0.1$, $\delta_{13}=0.5$ and $\Delta_{ab}=d_{Aa}=0$ are depicted in Fig. 7.15. As d_{ab} is made increasingly negative, an upper consolute curve appears at low temperatures, and a further decrease sees the emergence of a closed-loop. d_{ab} competes against the surfactant effect of the large value of $\delta_{13}=0.5$ so that the phase diagrams progress gradually from closed-loops to upper consolute curves.

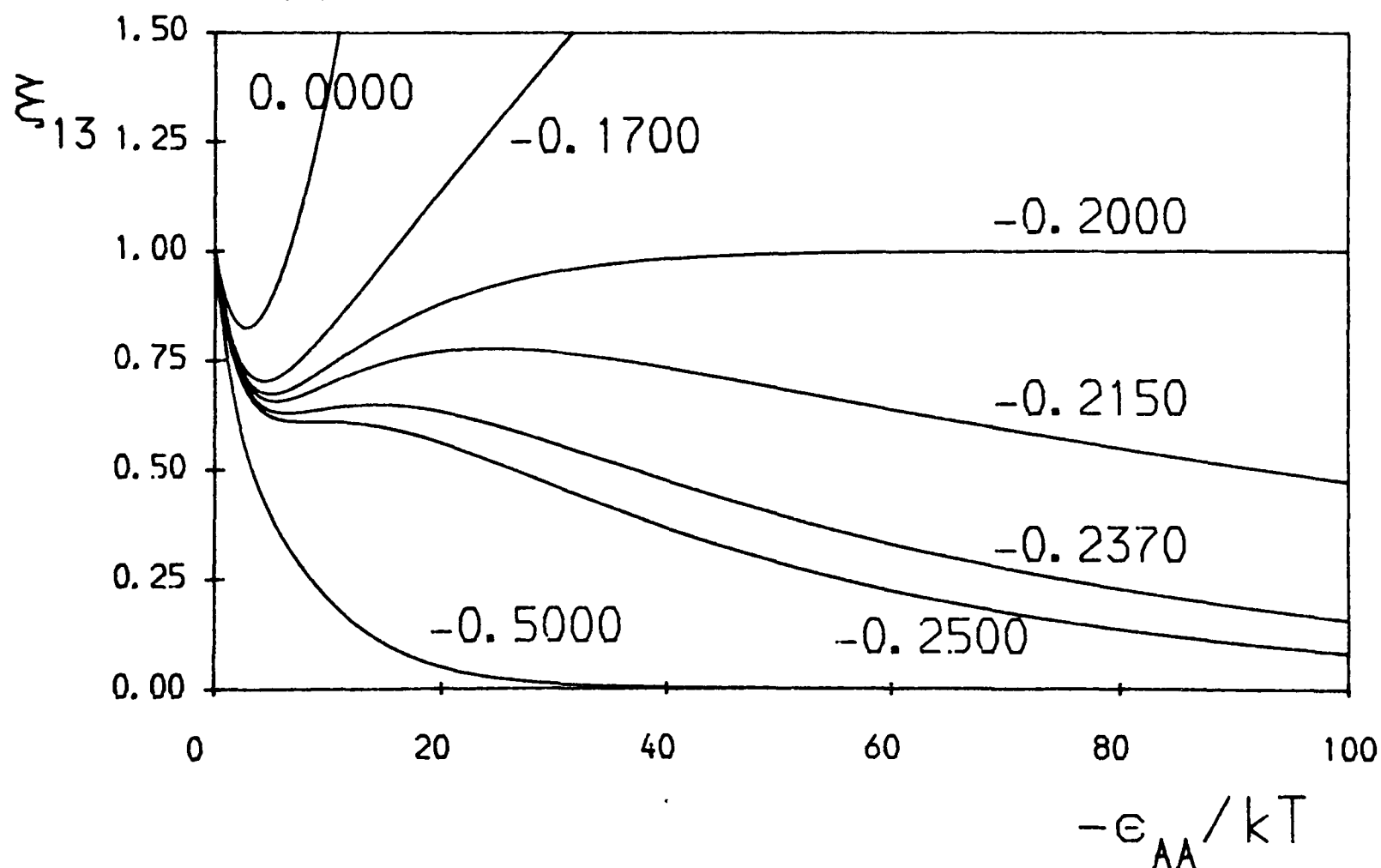


Fig. 7.14 The temperature dependence of ξ_{13} for an AA-ab mixture with $\Delta_{Aa}=-0.1$, $\delta_{13}=0.5$ and $\Delta_{ab}=d_{Aa}=0$. The values of d_{ab} are labelled on the curves.

d_{ab}	Upper Critical Point, $kT_c/-\epsilon_{AA}$	Lower Critical Point, $kT_c/-\epsilon_{AA}$	Upper Critical Point, $kT_c/-\epsilon_{AA}$
-0.2250	-	-	2.9685×10^{-2}
-0.2283	1.8284×10^{-1}	1.5412×10^{-1}	3.4831×10^{-2}
-0.2370	2.2499×10^{-1}	9.7257×10^{-2}	5.6313×10^{-2}
-0.2400	2.3345×10^{-1}	-	-

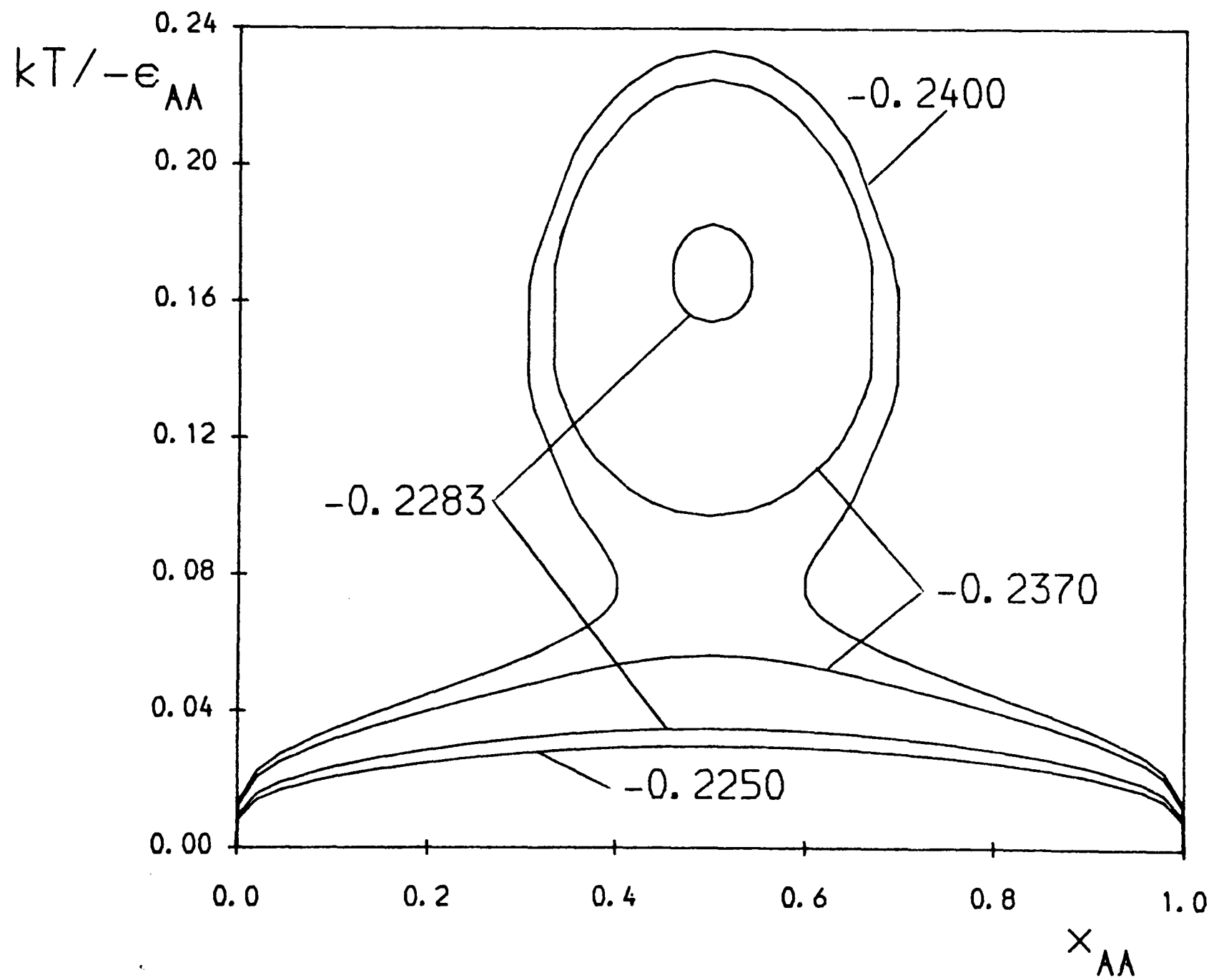


Fig. 7.15 Coexistence curves for an AA-ab mixture with $\Delta_{Aa}=-0.1$, $\delta_{13}=0.5$ and $\Delta_{ab}=d_{Aa}=0$ for $\xi_{13}^c=0.64183$. The values of d_{ab} are labelled on the curves.

7.3 CONCLUSION

Lattice mixtures of two bifunctional molecules AA and ab with finite interactions have been investigated. Robledo's exact thermodynamic correspondence between the lattice model and simpler spin systems was used to calculate the mixture's phase equilibria. The AA-ab mixtures can be used to model aqueous surfactant solutions where the AA molecule represents water and the ab molecule represents amphiphile. The mixtures of Section 7.2.5 with $\Delta_{Aa} > 0$ and $\delta_{13} = d_{ab} = \Delta_{ab} = d_{Aa} = 0$ showed the usual increase in immiscibility as the attractive forces between the unlike molecules AA and ab are decreased. When the molecule ab is given a surfactant character with $\delta_{13} = \epsilon_{Ab} - \epsilon_{Aa} < 0$, closed-loops were made possible. It must be noted that very specific intermediate values of the δ_{13} interactions were required (see Section 7.2.6). If ab is a poor surfactant with small negative values of δ_{13} then only an upper consolute curve is found, and if ab is a good surfactant with large negative values of δ_{13} then complete miscibility is seen. Furthermore, if the surfactant-surfactant forces are made stronger than the surfactant-water forces, then the closed-loops disappear. This was shown in Section 7.2.7 for large negative values of $d_{ab} = \epsilon_{bb} - \epsilon_{aa}$. In Sections 7.2.10-7.2.12 AA-ab mixtures with $\Delta_{Aa} < 0$ were investigated. The trends determined for these systems were similar to those for the systems with $\Delta_{Aa} > 0$ although the effect of δ_{13} was reversed; large positive values of δ_{13}

were required for closed-loop coexistence to be exhibited. The results of this chapter can provide an insight into the mechanisms of phase separation in the experimentally determined phase diagrams of aqueous surfactant solutions described in Chapter 8.

One can not help but notice that the coexistence curves obtained for the AA-ab mixtures are all symmetric about the critical value of $x_{AA}=1/2$, due to their correspondence with the spin-1/2 Ising model. Such symmetry does not exist in the highly skewed coexistence curves of real surfactant solutions: in the case of the closed-loop coexistence curves found experimentally for some aqueous solutions of nonionic surfactants, the lower critical point occurs at much lower compositions of surfactant than the upper critical point (see Section 8.1 of Chapter 8). Robledo [61] has described a correspondence between the spin-1 Ising model and a ternary mixture of bifunctional molecules AA, BB and ab. Furman et al. [68] have studied the spin-1 model in the mean-field approximation, and the system's global phase diagrams are known in detail. Consequently, the phase equilibria of ternary lattice mixtures of AA, BB and ab can also be determined. If the BB species of the mixture is taken to represent vacuum by setting its activity to zero, then we are left with a compressible mixture of AA and ab molecules. This mixture does not suffer from the symmetry restrictions of the spin-1/2 model so that the coexistence curves are expected to be more like those of the real systems. A systematic study of compressible mixtures of AA

and ab bifunctional molecules for different values of the interactions may provide an understanding of the highly asymmetric nature of the coexistence curves found in some micellar solutions.

Before concluding this chapter, a few more aspects of closed-loop coexistence must be discussed. The first calculations showing the existence of both upper and lower critical points were reported by Barker and Fock [69]. They investigated phase separations in a number of model mixtures of A and a molecules in which the molecular interactions depend on the relative orientation of the molecules by using the quasichemical approximation. With rising temperature, the entropy effects favouring random orientations of the molecules destroy the directional bonds, leading to phase separation and closed-loops. The symmetric loops obtained were very similar to those presented in this chapter. Decorated lattice models of A and B molecules have also been transformed exactly into the spin-1/2 model to give closed-loop coexistence curves [70],[71]. These lattice models have the built-in symmetry about $x=1/2$, but models lacking this inherent symmetry have also been investigated [72]. Furthermore, the phase diagrams for some of the A-B mixtures [73] exhibit a closed-loop coexistence curve together with a lower consolute curve found at lower temperatures; these features are very similar to those described in Section 7.2.7. Closed-loops are also seen with lattice gas models of mixtures of strongly interacting organic liquids [74],[75],[76],[77]. A progression from

complete immiscibility to closed-loop coexistence, and finally to upper consolute coexistence is seen as the interaction parameters are changed. In further work Goldstein [78] used a phenomenological approach based on the Flory-Huggins theory to determine asymmetric closed-loop coexistence curves for micellar solutions and microemulsions.

The closed-loops of Chapter 3 were obtained by making the attractive interactions in a system of pure spheres temperature dependent. Similar phase diagrams have also been calculated by Reatto and Tau [79] for systems of hard core molecules with temperature-dependent attractions. Goldstein [80] has used temperature-dependent attractions in a phenomenological model of surfactant-water mixtures incorporating hydrophobic interactions and the configurational entropy of the amphiphiles; the resulting phase diagrams are in good agreement with those found experimentally for aqueous solutions of nonionic surfactants. However, in general the temperature dependence of the water-water, the surfactant-surfactant, and the surfactant-water forces are not well known. A distinct advantage of the lattice model of AA and ab bifunctional molecules is that it does not require an explicit expression for the temperature dependence of the AA-AA, AA-ab, and ab-ab interactions. An asymmetry in the ab surfactant molecule's interactions with AA is sufficient to enable closed-loop coexistence curves.

CHAPTER 8

AQUEOUS MICELLAR SOLUTIONS

Surface-active agents or surfactants are generally understood to be soap-like or amphiphilic molecules containing both a hydrophilic and lipophilic group. The behaviour of a surfactant in water is quite different to that of an ordinary solute. As the term surface-active agent implies, these molecules modify the interfacial physics of the aqueous phase in which they are dispersed even at very low concentrations. However, the definitive attribute of surfactant molecules is their capacity to form micellar aggregates; the amphiphiles associate reversibly with each other to a highly exaggerated degree to form thermodynamically stable micellar solutions possessing colloidal dimensions.

Phase separations in aqueous micellar solutions of ionic, nonionic and zwitterionic surfactants have long been the subject of academic and industrial interest. Liquid crystalline phases are common in these systems at high concentrations of surfactant, and although they are extremely interesting in their own right, the present analysis will concentrate on the phase boundaries found at

lower concentrations. The existence of a miscibility gap within an isotropic solution region is a common phenomenon in two-component systems of non-amphiphilic compounds. Some micellar solutions also show phase boundaries on the temperature-composition phase diagram known as "cloud curves" where two micellar solutions are in coexistence. These miscibility gaps may represent regions of upper consolute coexistence with appropriate upper critical solution temperatures, or may involve lower consolute curves with lower critical points. Certain systems also exhibit closed-loop coexistence with both upper and lower critical solution temperatures.

Aqueous solutions of pure ionic surfactants do not possess cloud curves, but this type of phase separation is brought about by the addition of electrolyte. The cloud curves of nonionic amphiphiles comprised of an alkyl tail and a hydrophilic ethylene oxide headgroup have been studied extensively. The polyoxyethylene surfactants of the form $C_nH_{2n+1}(OCH_2CH_2)_mOH$, hereafter designated C_nE_m , give a rich variety of phase coexistence [3]. Zwitterionic surfactants have a separation of charge in the headgroup without dissociation, confirmed by the fact that the species do not enhance electrical conductivity in solution. These systems have been less investigated, but recent work [1],[81], has shown that these surfactants have cloud curves with upper critical end points and are thus amenable to theoretical modelling.

In contrast to and in spite of vigorous experimental activity directed toward a greater understanding of mixtures of water and surfactant, the theory of such systems has lagged far behind. Modelling of micellar systems requires detailed information about the micellar structure and about the complex molecular interactions that are at play. The investigation of the micelle's structure has received much attention recently [2],[82],[83], with detailed studies of changes in micellar shape and size as a function of temperature and composition. Spectroscopic techniques including nmr line-width and diffusion studies, light scattering, and small-angle neutron scattering have chiefly been used. The early hypothesis suggesting that the growth of the micelles was responsible for phase separation has been shown to be incorrect; although micellar growth does occur in some systems, micelles that remain small and closely spherical over a wide temperature and composition range also show cloud curve phase separation. Hence, a possible approximation for these systems involves the modelling of micelles as spheres of fixed size. The phase equilibria for a range of nonionic and, in particular, zwitterionic surfactants have been studied with the use of such a model.

First, a brief summary of theoretical work investigating the formation of spherical micelles in aqueous solutions of nonionic surfactants, C_nE_m , and the phase equilibria between two such micellar phases is undertaken. However, the bulk of the research involves an investigation of the upper

consolute coexistence found in micellar solutions of zwitterionic surfactants. The results of theoretical calculations are compared with the experimentally determined phase diagrams of the zwitterionics in Section 8.2.

8.1 NONIONIC SURFACTANT-WATER SYSTEMS

Aqueous systems comprising polyoxyethylene, C_nE_m , nonionic surfactants exhibit lower consolute cloud curves and closed-loops. Phase equilibrium studies in these micellar solutions [84],[85],[86] have shown that the micelles formed are often roughly spherical in shape and have a well-defined aggregation number, and that in the region of the cloud curve the two isotropic phases are micellar. These conclusions have been confirmed by the findings of recent light scattering and neutron scattering experiments [3],[87],[88], and also by nmr studies [2],[89]. However, the aggregates are continually exchanging particles with each other through a multitude of chemical equilibria, so the description of phase equilibria has an added complexity.

Phase separation in surfactant solutions has been studied within the context of lattice models in Chapter 7. Closed-loop coexistence curves similar to those observed experimentally were obtained when the surfactant character of one molecule was increased. An insight was given into the fine balance of the molecular interactions that is required for closed-loop coexistence to be exhibited.

However, because of the mapping onto the spin-1/2 Ising model, the lattice mixture's coexistence curves were symmetric. In contrast, the closed-loop phase diagrams obtained with the nonionic surfactants are highly asymmetric with the lower critical point at very low compositions of surfactant. Thus, the lattice model could only hope to describe the general qualitative features of the experimental phase diagrams. A study of a compressible lattice mixture of AA and ab bifunctional molecules allows for the possibility of asymmetric closed-loop coexistence curves, and could provide a further understanding of the mechanisms of phase separation in micellar solutions. It must be noted that some prescriptions of other decorated lattice models for mixtures of A and B molecules give rise to asymmetric closed-loop coexistence curves which provide an adequate fit of experimental data (see the conclusion of Chapter 7 and an article by Lang [90]).

Continuum approaches by Hayter and Zakauf [91], and Leng [93] have investigated the mechanism of phase separation in nonionic micellar solutions. Furthermore, a statistical theory by Reatto and Tau [79] has studied this cloud point transition for a pure hard core system with temperature-dependent attractive interactions. The low value of the lower critical point concentration was explained by the presence of an extended repulsive intermicellar interaction due to a region of structured water. This leads to an effective repulsive inter-micellar interaction which is temperature dependent due to the

disruptive effect of thermal motion; at a particular temperature the water structure is destroyed with a sharp rise in the inter-micellar attractive interaction and phase separation. Excellent agreement was found for the aqueous solutions of polyoxyethylene surfactants. Indeed, various experimental studies [2],[89] have revealed a lessening of the solvation of the ethylene oxide chains with increasing temperature, possibly due to the disruption of hydrogen bonds. These findings are consistent with the results of Section 3.5 in Chapter 3 for a system of pure hard spheres described by the Carnahan-Starling equation with a simple temperature dependence of the attractions. It was shown that a sharp rise in the attractive interactions between the spheres was required for closed-loop coexistence to be exhibited.

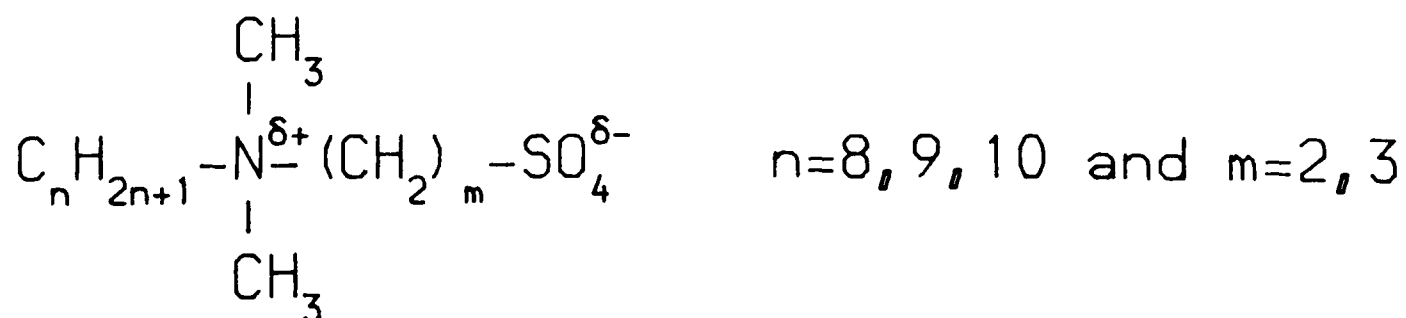
None of the theories discussed so far has treated the association of the amphiphiles explicitly. Goldstein [80] has investigated the formation of spherical micelles in aqueous solutions of nonionic surfactants with a phenomenological model which incorporates size distributions of the micellar species. Again the model attributes the experimentally observed lower critical solution points in these systems to surfactant-water hydrogen bonding, whose temperature dependence is described with a mean-field approximation. A qualitative agreement between the calculated phase diagrams and the experimental closed-loops was achieved. Goldstein's work in conjunction with the other studies mentioned in this section have greatly

increased our understanding of the phase separation in aqueous solutions of nonionic surfactants.

8.2 ZWITTERIONIC SURFACTANT-WATER SYSTEMS

In Chapters 4 and 5 the phase equilibria of binary mixtures of small and large spheres were determined for different values of the molecular interactions and, in particular, for various size differences. General features of these calculations may be compared with the phase separation of spherical micelles in water where the size ratios may be of the order of $d_2/d_1=20/1$. The theoretically calculated phase diagrams for systems with large differences in size showed regions of liquid-liquid immiscibility ending at upper critical end points. Coexistence of two micellar solutions with upper consolute points have been observed experimentally for zwitterionic surfactants with betaine sulphate and sulphonate headgroups. Consequently, these solutions of spherical micelles are amenable to theoretical modelling.

The amphiphiles of interest are the zwitterionic betaine sulphate surfactants which have a lipophilic alkyl chain and a hydrophilic zwitterionic group.



Two surfactants of this class have been investigated: when $m=2$ the surfactant is denoted C_nEtSO_4 , and when the ethyl group is replaced by a propyl group $m=3$, the surfactant is C_nPrSO_4 . Another related zwitterionic surfactant is C_nPrSO_3 where the sulphate group has been replaced by a sulphonate group.

These zwitterionic surfactant-water systems display liquid-liquid miscibility gaps delineated by upper consolute boundaries with upper critical solution temperatures in the range $0-100^{\circ}C$; the aqueous phase diagrams have recently been investigated [1],[81]. The most detailed cloud curves are for the C_nPrSO_4 series with $n=8,9,10$, and for C_nEtSO_4 with $n=9$ and 10 , while approximate boundaries have been determined for C_nPrSO_3 with $n=12,14$ and 16 .

Fig. 8.1 depicts the partial phase diagram of $C_{10}EtSO_4$ with the weight percents of surfactant in the coexisting micellar phases plotted as a function of temperature. The upper consolute boundaries for C_nPrSO_4 systems with $n=8,9,10$ are seen in Fig. 8.2. The experimental phase diagrams show that the miscibility gap increases in each series as the length of the lipophilic alkyl chain n is increased. For a fixed value of n the extent of liquid-liquid immiscibility is far greater when the surfactant has a sulphate SO_4 group, than when it comprises a sulphonate SO_3 group. This trend is similar for the two surfactant series C_nEtSO_4 and C_nPrSO_4 , although the surfactants incorporating the propyl group C_nPrSO_4 have slightly increased miscibility gaps.

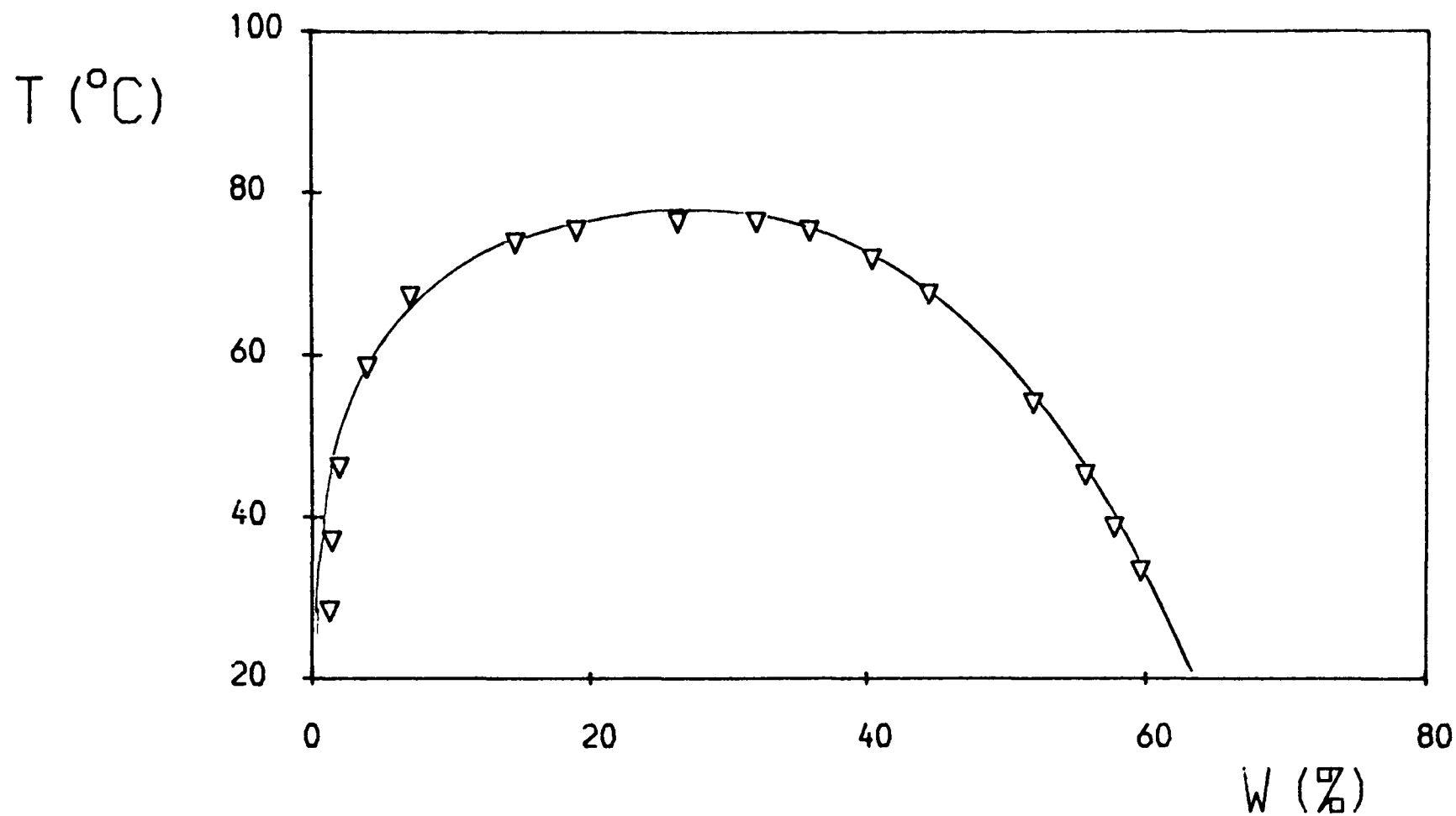


Fig. 8.1 Partial phase diagram for a zwitterionic $C_{10}EtSO_4$ surfactant-water system.

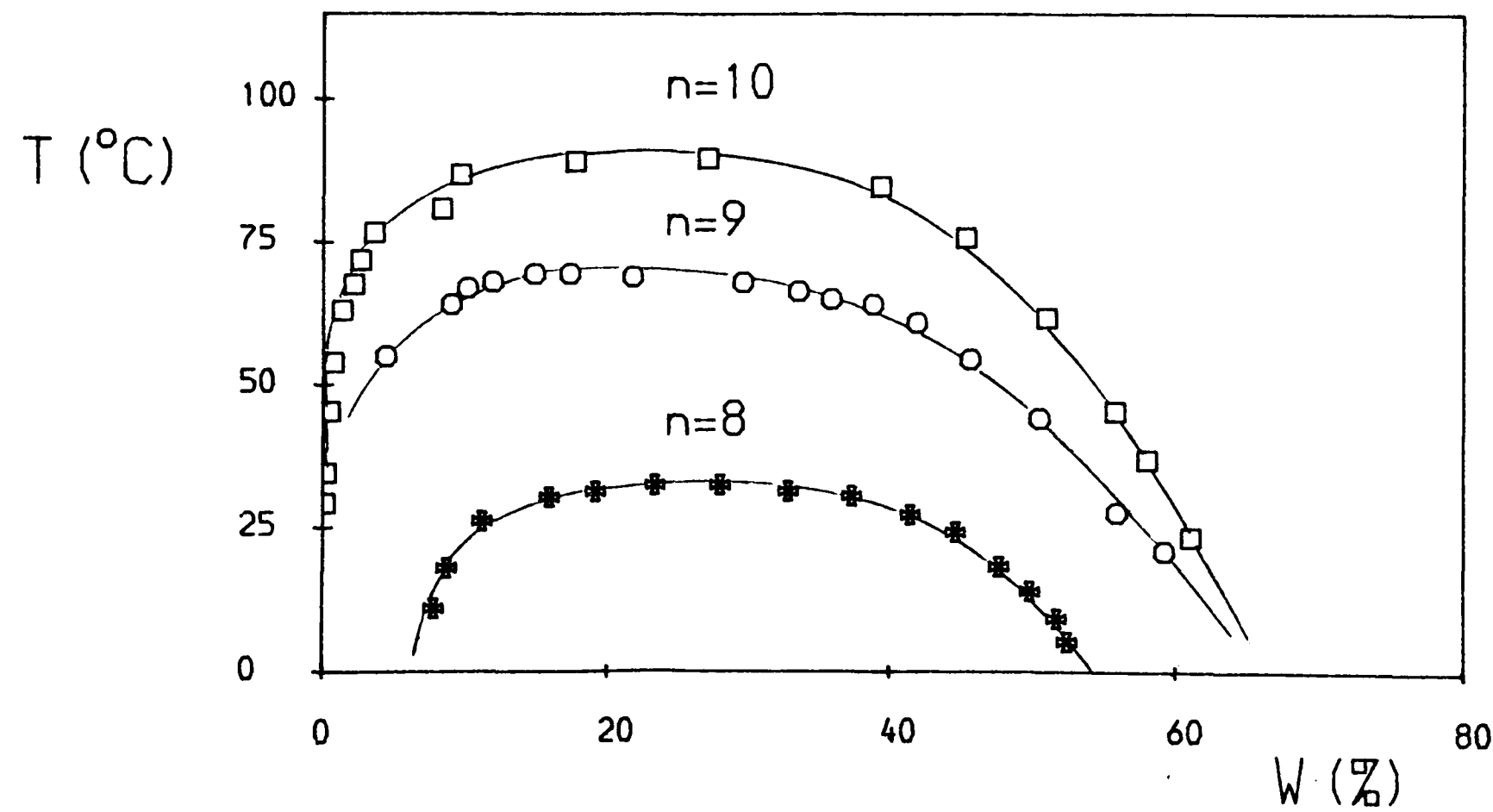


Fig. 8.2 Partial phase diagrams for zwitterionic C_nPrSO_4 surfactant-water systems.

Light scattering measurements of dilute solutions of C_nPrSO_3 above the upper critical point indicate that small spherical micelles are formed for the shorter chain lengths [92]. These findings are consistent with the evidence of the structure of the lyotropic liquid crystalline phase I_1 formed at higher surfactant concentrations, which is composed of a cubic array of small spherical micelles. Light scattering measurements for aqueous solutions of $C_{10}EtSO_4$ also show small spherical micelles [93],[94]. Furthermore, Nilsson et al. [1] have reported nmr line-width and diffusion studies for C_9PrSO_4 showing that above the critical micellar concentration (about 0.05 M), aqueous solutions of these surfactants form small spherical micellar aggregates which retain their identity over a wide range of concentrations and temperatures. One can conclude that for these zwitterionic surfactant-water mixtures the micelles may be modelled by rigid spheres, and thus these systems are suitable for comparison with the theoretical results of Chapters 4 and 5.

A substantial degree of agreement is seen when the appropriate links between experiment and theory are made. The effect of varying the size difference in a binary mixture of hard core molecules with fixed attractive interactions was summarized in Fig. 5.15 of Chapter 5. Fig. 5.15 represents temperature-density projections of the upper consolute curves representing regions of liquid-liquid immiscibility, obtained for mixtures of large (2) and small (1) spheres with $a_{11}=0$ and $a_{12}=a_{22}/2$. It is clear that for

these hard core mixtures, the larger the solute-solvent size difference, the greater the extent of liquid-liquid immiscibility. To relate this to experiment, we compare the cloud curves of micelles with the same headgroups (such as PrSO_4) so that the attractive interaction between unlike molecules a_{12} is fixed, and vary the alkyl chain C_n . The trend observed in the model systems is seen experimentally with the zwitterionic systems of Fig. 8.2. When the $C_n\text{PrSO}_4$ amphiphile's hydrophobic alkyl chain is lengthened from $n=8$ carbon atoms to $n=9$ and then to $n=10$, larger spherical micelles are formed corresponding to an increase in the solute-to-solvent size ratio. The larger size ratio is in turn accompanied by an increase in the area spanned by the miscibility gap, and the maximum cloud temperature corresponding to T^{UCEP} increases for each of the surfactant series as n increases.

Because the densities of the surfactant and the aqueous surfactant solution are virtually the same, the weight percent of surfactant in solution is equivalent to the volume fraction (reduced density, η). Hence, the zwitterionic coexistence curves can be compared quantitatively with the theoretical curves obtained for mixtures of hard cores. It was shown in Fig. 5.15 that the upper critical end point temperature T^{UCEP} of the model system varies substantially with size ratio; T^{UCEP} decreases from its maximal value at an infinite size ratio as the size difference is decreased. However, the values of the upper critical end point densities η_2^{UCEP} are almost constant but

increase slowly as the size difference is decreased. This result is also in agreement with experiment. In the case of the $C_n\text{PrSO}_4$ -water system η_2^{UCEP} decrease steadily as n is increased with values of $\eta_2^{\text{UCEP}}=0.22, 0.23$ and 0.26 for $n=8, 9$, and 10 respectively (these values were estimated using rectilinear diameters). The trend found with micellar solutions of nonionic surfactants is more marked.

The experimental data of Figs. 8.1 and 8.2 are scaled with respect to the UCEP temperature and weight percent in Fig. 8.3: the triangles represent $C_{10}\text{EtSO}_4$, the squares $C_{10}\text{PrSO}_4$, the circles $C_9\text{PrSO}_4$, and the crosses $C_8\text{PrSO}_4$.

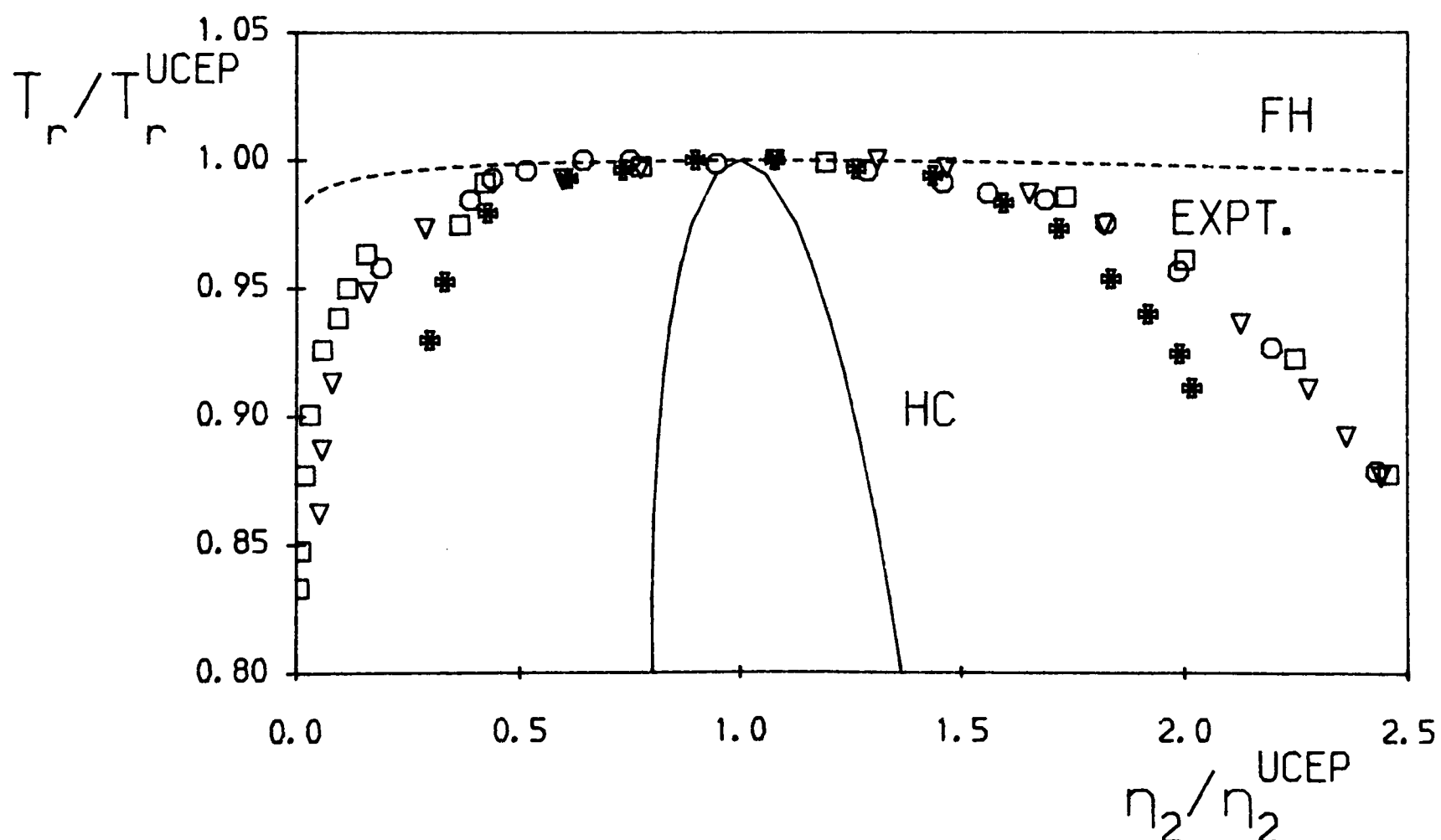


Fig. 8.3 The scaled zwitterionic phase diagrams are compared with the curves obtained using the hard core equation (HC) and the Flory-Huggins (FH) theory.

As with the theoretical results presented in Fig. 5.16, good scaling is achieved by three of the systems with slightly poorer scaling for the system C_8PrSO_4 ; the theoretical results do not scale as well as the experimental data because the variations in size are much greater. The zwitterionic curves are compared in Fig. 8.3 with the scaled curve HC obtained for a binary mixture of points and hard cores (see Section 4.8.2) and also with the coexistence curve FH calculated using the Flory-Huggins polymer solution theory [95] for $M=8000$. The experimental curves are substantially broader than the theoretical curve for the point-hard core mixture which represents an infinite size ratio. In contrast, the Flory-Huggins theory predicts a curve which is much broader than those obtained experimentally for the zwitterionic surfactant-water systems. Clearly, the Flory-Huggins theory is not appropriate for the spherical micelles considered here.

It is useful at this stage to summarize the quantitative differences in the results of the calculations for the interactions chosen, and the experimental micellar data that have emerged. The calculated coexistence curves have higher values of η_2^{UCEP} than those found experimentally with differences close to a factor of two. In addition to the crude form of the potentials chosen, the level of approximation in the mean-field theory may be part of the cause of this difference. In fact, perturbation theory calculations of the phase separation in colloidal systems using the DLVO potential of mean force for a one-component

model [96],[97], have shown that the density of the lower critical point in this case decreases significantly as the accuracy of the perturbation theory increases. Another major difference between the theoretical results and experiment is that the calculated miscibility gaps are narrower than the measured cloud curves.

In Chapter 4 binary mixtures of point particles and attracting spheres were investigated for different values of the point-sphere a_{12} attractive interaction. The comparison of the changes in phase separation of micelles with fixed hydrophobic chains (fixed n) but differing headgroups turns out to be more difficult than an analysis of the effects of size. As well as changing the a_{12} attractive interactions, changing the surfactant's headgroup probably also affects the micelle's size and shape. This is due to the dominating influence of the intramicellar headgroup interaction in determining the form of the surfactant aggregate. However, one experimental example can be discussed: the fact that the replacement of the dimethyl ammonio group by a diethyl ammonio unit caused a reduction in immiscibility with lower upper critical temperatures was said to be perplexing [1]. Considered in terms of the usual ideas of binary mixtures, this change would be expected to weaken the attraction between water and the more hydrophobic molecule (a_{12} decreasing) and thus increase the extent of liquid-liquid immiscibility. However, in light of the results presented for the point-hard core mixtures, a decrease in the surfactant-water attractions (decrease in a_{12}) by changing

the methyl groups to ethyl groups with a corresponding decrease in the liquid-liquid miscibility gap does not seem so odd.

The phase equilibria of model mixtures of spheres of different sizes can also be compared directly with the upper portion of the closed-loop miscibility gaps found for aqueous solutions of the nonionic surfactants (see Section 8.1). Again the density at the calculated upper consolute point η_2^{UCEP} is higher than experimentally obtained values but general trends are in agreement: an increase in the solute-to-solvent size ratio corresponding to an increase in micellar size is accompanied by an increase in the extent of liquid-liquid immiscibility. It must be noted that relatively few measurements are available for the top of the closed-loop as this occurs at temperatures well above 100°C. The values of the reduced density at the lower critical end point η_2^{LCEP} for aqueous solutions of polyoxyethylene surfactants may be very low (<0.01) and show large changes with the molecular structure of the surfactant.

Before the survey of the upper consolute curves occurring in aqueous zwitterionic surfactant solutions is concluded, another theory of phase separation in micellar systems is worth a mention. A thermodynamic theory of phase separation in self-associating micellar solutions has been presented by Blankschtein et al. [98]. This approach incorporates a distribution of micellar aggregates controlled by multiple chemical equilibrium, and also a mean-field description of

interactions between aggregates. The upper consolute curves obtained were in excellent agreement with experimental findings in aqueous micellar solutions of dioctanoyl-phosphatidylcholine (C₈-lecithin) and water. In this section the zwitterionic cloud curves are modelled using this approach. Three input parameters are required: the temperature T_c and weight fraction $W_c(\%)$ of the critical point, and the ratio of the effective volumes of the surfactant and water molecules $\Omega = v_s/v_w$. Ω can be approximated as a molecular weight ratio of the surfactant and water molecules. The resulting coexistence curves are shown in Fig. 8.4 for the zwitterionic surfactant series C_nPrSO₄ with n=8, 9, and 10.

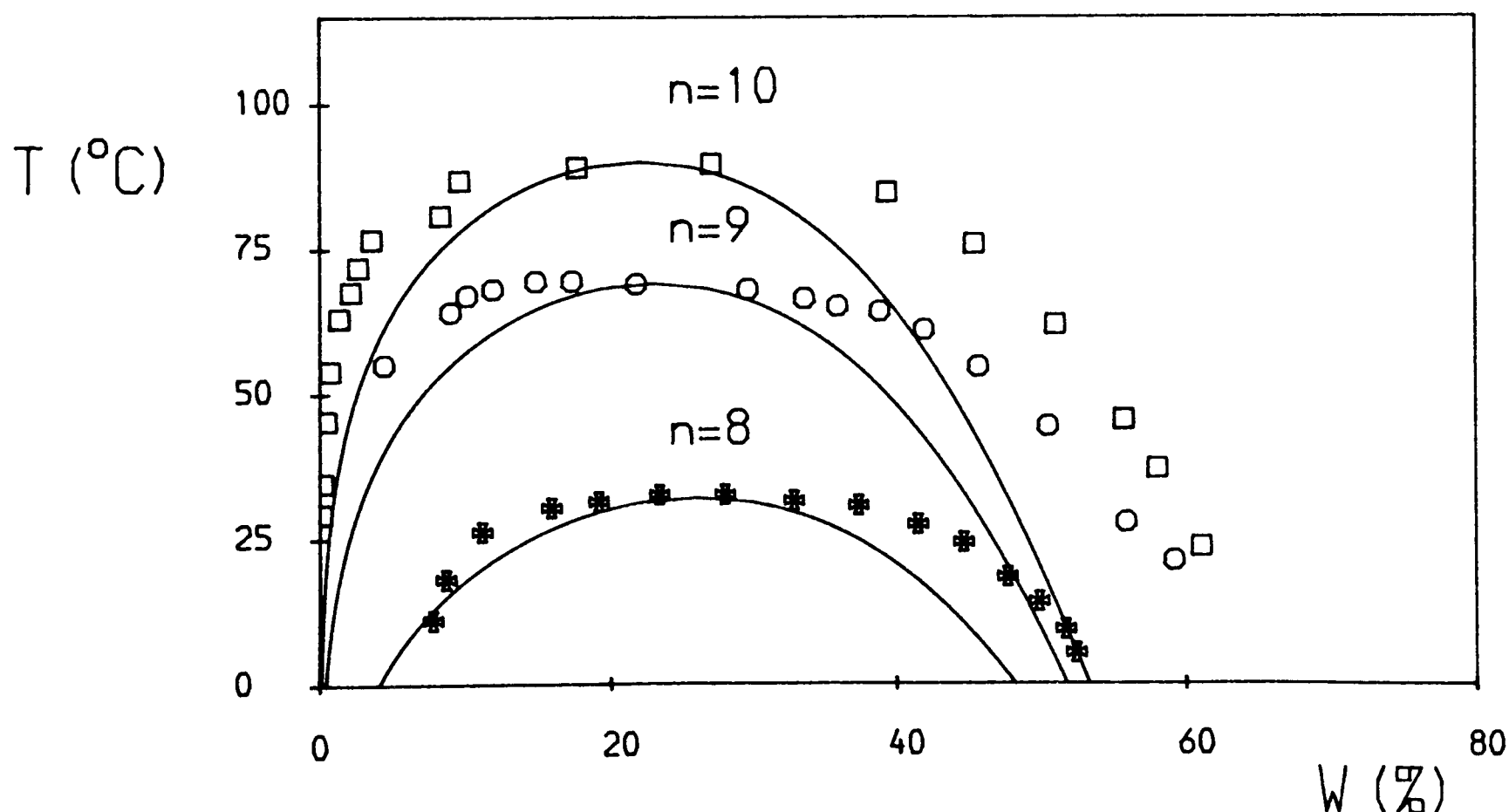


Fig. 8.4 The zwitterionic phase diagrams for C_nPrSO₄ are compared with coexistence curves obtained using the approach of Blankschtein et al. (solid curves).

The following input parameters were used: C_8PrSO_4 $T_C=32.5^{\circ}C$, $W_C(\%)=0.26$, $\Omega=295/18=16.4$; C_9PrSO_4 $T_C=69.4^{\circ}C$, $W_C(\%)=0.23$, $\Omega=309/18=17.2$; $C_{10}PrSO_4$ $T_C=90.0^{\circ}C$, $W_C(\%)=0.22$, $\Omega=323/18=17.9$. The curves obtained from the theory were not in very good agreement with the experimental cloud curves. A good fit is only obtained if Ω is used as a free parameter, and unrealistically small values of the parameter were required, corresponding to large micellar aggregation numbers. The theory seems to fail because it was developed for aggregates which grow considerably in size, such as the long rod-like micelles formed by aqueous solutions of C₈-lecithin. However, as pointed out earlier the micelles formed by the zwitterionic surfactants are small and spherical.

8.3 CONCLUSION

A detailed understanding of micellar phase separation was not the immediate goal of the research. A quantitative comparison of micellar cloud curves with theory is not possible at this time owing to the insufficient information available for surfactant systems. The forms of the potentials for the micelle-water and micelle-micelle interactions are not known, and generally micellar sizes and shapes are not available. The problem is addressed in two parts which involve an understanding of the complex intermolecular forces which are at play, and the effect of the large size difference. Chiefly, this research has been

considering the latter of the two problems.

Phase boundaries have been calculated in previous chapters for model binary mixtures comprising spheres of different sizes between which there are long-ranged attractive forces. Particular attention was paid to mixtures of point particles and hard cores which represent an infinite size ratio. The systems showed a wide variety of behaviour that included liquid-liquid and gas-gas immiscibility, and the formation of negative azeotropes. The dependence of the liquid-liquid immiscibility on the molecular interactions, and more particularly on the size difference has enabled a comparison with the trends found in aqueous surfactant solutions; the model systems are shown to reproduce some of the behaviour of micellar solutions if it is assumed that the large spheres are models of the micelles and the small spheres represent solvent. A very good qualitative agreement between the theoretically calculated phase diagrams and the experimentally observed cloud curves of aqueous micellar solutions of zwitterionic surfactants has been established.

Furthermore, a fundamental study of surfactant properties was undertaken in Chapter 7 for lattice mixtures of AA and ab bifunctional molecules. An asymmetric surfactant-like interaction of molecules ab with molecules AA was found to be sufficient for closed-loop coexistence curves to be present in the phase diagrams of such mixtures. The curves were qualitatively similar to those found experimentally with aqueous solutions of nonionic

surfactants, and future research for a compressible AA-ab lattice mixture should improve matters considerably.

Our biochemical and genetical understanding of the processes involved in molecular synthesis have advanced enormously in recent years. However, only primitive ideas are presently available as to how linearly synthesised molecules form the molecular aggregates that are cellular structures. The study of micellar systems bridges the gap between the well-established theories of simpler molecular assemblies and the waste-lands of biological systems. A clearer understanding of the mechanisms of self-assembly in aqueous solutions of amphiphilic compounds should provide a route to these more complicated systems. Thankfully, a promising future in this line of research is in sight.

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APPENDIX I

NPT MONTE CARLO SIMULATIONS OF BINARY HARD SPHERE MIXTURES

d_2/d_1	x_2	ξ	Pd_1^3/kT	Z	Z^{CV}	$(Z-Z^{CV})/Z$
5/3	0.1019	0.4530	5.430	8.596	8.815	-2.49%
5/3	0.1019	0.4993	8.308	11.93	11.86	+0.60%
5/3	0.1019	0.5410	11.82	15.67	15.80	-0.86%
5/3	0.1019	0.5879	20.68	25.22	22.45	+12.3%
5/3	0.5000	0.4448	2.580	8.549	8.189	+4.39%
5/3	0.5000	0.4982	3.943	11.66	11.48	+1.57%
5/3	0.5000	0.5271	5.125	14.33	13.97	+2.56%
5/3	0.5000	0.5899	9.790	24.46	22.20	+10.2%
5/3	0.8981	0.4817	2.388	11.06	11.22	-1.44%
5/3	0.8981	0.5264	2.841	12.04	15.20	-20.8%
5/3	0.8981	0.5577	4.054	16.22	19.06	-14.9%
5/3	0.8981	0.6078	7.126	26.15	28.23	-7.35%
3/1	0.06481	0.4515	1.977	6.156	6.229	-1.17%
3/1	0.06481	0.4951	2.938	8.343	8.020	+4.02%
3/1	0.06481	0.5455	4.451	11.47	11.04	+3.91%
3/1	0.06481	0.5968	6.932	16.33	15.86	+2.96%
3/1	0.5000	0.3081	1.424×10^{-1}	3.387	3.316	+2.12%
3/1	0.5000	0.5525	9.926×10^{-1}	13.17	13.46	-2.19%
3/1	0.5000	0.5860	1.362	17.03	17.19	-0.92%
3/1	0.8981	0.4878	4.409×10^{-1}	11.53	11.31	+1.95%
3/1	0.8981	0.5581	6.854×10^{-1}	15.66	18.47	-15.2%
3/1	0.8981	0.6009	1.203	25.52	25.74	-0.86%
5/1	0.1019	0.4478	2.578×10^{-1}	4.108	4.047	+1.51%
5/1	0.1019	0.5051	3.944×10^{-1}	5.572	5.375	+3.66%
5/1	0.1019	0.5575	6.229×10^{-1}	7.974	7.227	+10.3%
5/1	0.5000	0.09955	4.130×10^{-3}	1.369	1.360	+0.60%
5/1	0.5000	0.3016	2.690×10^{-2}	2.942	2.979	-1.23%
5/1	0.5000	0.5000	1.286×10^{-1}	8.481	8.484	-0.04%
5/1	0.5000	0.5747	1.962×10^{-1}	11.26	14.02	-19.7%
5/1	0.8981	0.4500	6.694×10^{-2}	8.753	8.752	+0.02%
5/1	0.8981	0.5009	1.026×10^{-1}	12.05	12.15	-0.81%
5/1	0.8981	0.5657	1.755×10^{-1}	18.25	19.24	-5.15%
20/1	0.1019	0.3387	1.584×10^{-3}	1.997	1.975	+1.12%
20/1	0.1019	0.4493	3.000×10^{-3}	2.852	2.816	+1.26%
20/1	0.1019	0.5024	4.500×10^{-3}	3.826	3.477	+10.0%
20/1	0.1019	0.5178	5.570×10^{-3}	4.594	3.719	+23.5%
20/1	0.1019	0.5569	9.500×10^{-3}	7.287	4.476	+62.8%
20/1	0.5000	0.09859	6.331×10^{-5}	1.345	1.320	+1.87%
20/1	0.5000	0.3004	3.941×10^{-4}	2.748	2.757	-0.30%
20/1	0.5000	0.4797	1.499×10^{-3}	6.543	6.795	-3.71%
20/1	0.5000	0.5166	1.832×10^{-3}	7.429	8.513	-12.7%
20/1	0.5000	0.5681	2.785×10^{-3}	10.27	12.03	-14.6%
20/1	0.8981	0.3495	4.510×10^{-4}	4.855	4.832	+0.47%
20/1	0.8981	0.4938	1.452×10^{-3}	11.06	11.44	-3.26%
20/1	0.8981	0.5651	2.470×10^{-3}	16.44	18.89	-13.0%

These results are for systems with a total of 108 particles in a cubic box. d_2/d_1 is the diameter ratio, x_2 is the composition of species 2, ξ is the total reduced density, Pd_1^3/kT is the reduced pressure, and $Z=PV/NkT$ is the compression factor. Z^{CV} is the corresponding value of the compression factor calculated using the Mansoori equation.

APPENDIX II

MOLECULAR DYNAMICS SIMULATIONS OF BINARY HARD SPHERE MIXTURES

d_2/d_1	x_2	ξ	z	z^{CV}	$(z-z^{CV})/z$	D_1	D_2
5/3	0.1019	0.4500	8.720	8.653	+0.77%	3.37×10^{-1}	1.62×10^{-1}
5/3	0.1019	0.4800	10.50	10.45	+0.48%	1.84×10^{-1}	8.92×10^{-2}
5/3	0.1019	0.5000	12.07	11.92	+1.30%	1.62×10^{-1}	5.56×10^{-2}
5/3	0.1019	0.5100	12.84	12.74	+0.80%	1.32×10^{-1}	3.33×10^{-2}
5/3	0.1019	0.5200	13.70	13.64	+0.43%	8.71×10^{-2}	3.93×10^{-2}
5/3	0.1019	0.5400	15.78	15.70	+0.55%	5.95×10^{-2}	2.70×10^{-2}
5/3	0.1019	0.5879	23.58	22.45	+5.01%	5.30×10^{-2}	1.38×10^{-3}
5/3	0.5000	0.4500	8.552	8.451	+1.19%	8.48×10^{-1}	3.58×10^{-1}
5/3	0.5000	0.4800	10.25	10.20	+0.45%	5.60×10^{-1}	2.48×10^{-1}
5/3	0.5000	0.5000	11.77	11.62	+1.32%	3.12×10^{-1}	2.06×10^{-1}
5/3	0.5000	0.5100	12.60	12.42	+1.36%	2.86×10^{-1}	1.67×10^{-1}
5/3	0.5000	0.5200	13.41	13.30	+0.84%	2.54×10^{-1}	8.70×10^{-2}
5/3	0.5000	0.5400	15.55	15.29	+1.66%	1.68×10^{-1}	5.40×10^{-2}
5/3	0.5000	0.5899	23.37	22.20	+5.28%	2.14×10^{-2}	7.38×10^{-3}
5/3	0.8981	0.4800	11.02	11.10	-0.70%	7.84×10^{-1}	3.02×10^{-1}
5/3	0.8981	0.5000	12.60	12.67	-0.60%	6.91×10^{-1}	1.83×10^{-1}
5/3	0.8981	0.5100	13.40	13.56	-1.17%	4.69×10^{-1}	1.45×10^{-1}
5/3	0.8981	0.5200	14.37	14.53	-1.09%	4.87×10^{-1}	1.31×10^{-1}
5/3	0.8981	0.5300	13.12	15.59	-15.8%	8.73×10^{-2}	1.68×10^{-2}
5/3	0.8981	0.5400	13.88	16.75	-17.1%	6.43×10^{-2}	3.55×10^{-3}
5/3	0.8981	0.5577	15.37	19.06	-19.4%	1.04×10^{-2}	1.25×10^{-3}
5/3	0.8981	0.6000	22.92	26.49	-13.5%	4.38×10^{-3}	2.79×10^{-4}
3/1	0.0648	0.5968	16.44	15.86	+3.68%	1.23×10^{-1}	4.77×10^{-3}
3/1	0.5000	0.5860	16.19	17.19	-5.80%	6.28×10^{-1}	1.75×10^{-3}
3/1	0.8981	0.4500	8.882	8.883	-0.02%	7.69	1.69
3/1	0.8981	0.5000	12.20	12.26	-0.52%	4.17	6.51×10^{-1}
3/1	0.8981	0.5100	12.92	13.12	-1.50%	3.25	4.20×10^{-1}
3/1	0.8981	0.5200	13.48	14.05	-4.09%	3.13	3.21×10^{-1}
3/1	0.8981	0.5300	14.92	15.07	-0.99%	2.62	2.72×10^{-1}
3/1	0.8981	0.5400	13.94	16.18	-13.9%	1.58	4.10×10^{-2}
3/1	0.8981	0.6009	26.68	25.74	+3.64%	8.18×10^{-1}	1.47×10^{-3}
5/1	0.1019	0.5300	6.384	6.158	+3.67%	3.79	2.02×10^{-1}
5/1	0.1019	0.5575	7.817	7.227	+8.17%	2.74	1.64×10^{-1}
5/1	0.5000	0.4500	6.217	6.299	-1.30%	2.63×10	3.13
5/1	0.5000	0.5000	8.123	8.484	-4.26%	1.60×10	1.16
5/1	0.5000	0.5200	8.878	9.631	-7.82%	1.52×10	4.15×10^{-1}
5/1	0.5000	0.5300	9.205	10.28	-10.5%	1.13×10	2.75×10^{-1}
5/1	0.5000	0.5747	12.02	14.02	-14.3%	6.28	3.42×10^{-2}
5/1	0.8981	0.4500	8.742	8.753	-0.12%	2.37×10	4.49
5/1	0.8981	0.5009	12.11	12.15	-0.35%	2.26×10	1.94
5/1	0.8981	0.5100	12.84	12.92	-0.60%	1.18×10	1.42
5/1	0.8981	0.5300	14.69	14.84	-1.00%	2.00×10	7.27×10^{-1}
5/1	0.8981	0.5400	13.26	15.93	-16.7%	1.48×10	1.60×10^{-1}
5/1	0.8981	0.5657	17.26	19.24	-10.3%	6.69	7.49×10^{-2}

d_2/d_1	x_2	ξ	z	z^{cv}	$(z-z^{cv})/z$	D_1	D_2
20/1	0.1019	0.5178	4.691	3.719	+26.1%		
20/1	0.1019	0.5580	7.153	4.502	+58.9%	1.85×10^2	4.02
20/1	0.5000	0.3500	3.460	3.442	+0.52%	1.28×10^3	1.72×10^2
20/1	0.5000	0.4000	4.377	4.391	-0.32%	7.95×10^2	7.96×10
20/1	0.5000	0.4500	5.629	5.730	-1.76%	6.71×10^2	5.75×10
20/1	0.5000	0.4900	6.824	7.223	-5.52%	5.36×10^2	2.53×10
20/1	0.5000	0.5000	6.985	7.676	-9.00%	6.63×10^2	1.35×10
20/1	0.5000	0.5100	7.032	8.167	-13.9%	6.09×10^2	4.23
20/1	0.5000	0.5166	7.546	8.513	-11.4%	5.73×10^2	8.35
20/1	0.5000	0.5523	9.068	10.78	-15.9%		
20/1	0.5000	0.5681	9.947	12.03	-17.3%	4.29×10^2	2.02
20/1	0.8981	0.4500	8.655	8.640	+0.17%	9.94×10^2	6.76×10
20/1	0.8981	0.4938	11.37	11.44	-0.58%	8.41×10^2	3.63×10
20/1	0.8981	0.5100	12.49	12.75	-1.98%	6.30×10^2	2.45×10
20/1	0.8981	0.5200	13.11	13.65	-3.98%	7.38×10^2	1.61×10
20/1	0.8981	0.5300	14.44	14.64	-1.32%	4.69×10^2	1.11×10
20/1	0.8981	0.5400	13.48	15.72	-14.2%	4.15×10^2	6.43×10^{-1}
20/1	0.8981	0.5651	16.39	18.89	-13.3%	2.55×10^2	1.41

These results are for systems with a total of 108 particles in a cubic box. d_2/d_1 is the diameter ratio, x_2 is the composition of species 2, ξ is the total reduced density, and $Z=PV/NkT$ is the compression factor. z^{cv} is the corresponding value of the compression factor calculated using the Mansoori equation. The self diffusion coefficients of species 1, D_1 , and species 2, D_2 , are given in terms of the units d_1^2/t , where d_1 is the diameter of species 1 and t is the absolute time. Note that both species are of equal mass, $m_1=m_2=1.0$.

APPENDIX III

THE VAPOUR PRESSURE CURVE FOR THE PURE HARD CORE SYSTEM

T_r	P_r	η_g	η_l	$r=\eta_l/\eta_g$
1.000000	1.000000	0.130444	0.130444	1.00000
0.990000	0.952185	0.0998324	0.164200	1.64476
0.980000	0.905783	0.0881094	0.179093	2.03262
0.970000	0.860785	0.0795111	0.190886	2.40075
0.960000	0.817180	0.0725387	0.201080	2.77203
0.950000	0.774957	0.0666116	0.210254	3.15642
0.940000	0.734105	0.0614317	0.218708	3.56018
0.930000	0.694612	0.0568219	0.226618	3.98822
0.920000	0.656465	0.0526668	0.234101	4.44495
0.910000	0.619653	0.0488860	0.241237	4.93468
0.900000	0.584160	0.0454212	0.248084	5.46186
0.890000	0.549972	0.0422282	0.254688	6.03123
0.880000	0.517076	0.0392726	0.261082	6.64795
0.870000	0.485455	0.0365271	0.267295	7.31771
0.860000	0.455094	0.0339696	0.273349	8.04686
0.850000	0.425975	0.0315818	0.279262	8.84251
0.840000	0.398081	0.0293482	0.285051	9.71270
0.830000	0.371394	0.0272560	0.290727	10.6665
0.820000	0.345895	0.0252940	0.296304	11.7144
0.810000	0.321564	0.0234526	0.301791	12.8681
0.800000	0.298381	0.0217232	0.307196	14.1413
0.790000	0.276325	0.0200987	0.312527	15.5496
0.780000	0.255374	0.0185722	0.317791	17.1111
0.770000	0.235506	0.0171381	0.322995	18.8466
0.760000	0.216696	0.0157910	0.328143	20.7804
0.750000	0.198922	0.0145261	0.333242	22.9409
0.740000	0.182158	0.0133390	0.338294	25.3612
0.730000	0.166377	0.0122259	0.343306	28.0803
0.720000	0.151555	0.0111829	0.348280	31.1440
0.710000	0.137664	0.0102067	0.353221	34.6067
0.700000	0.124675	0.00929415	0.358131	38.5330
0.690000	0.112560	0.00844221	0.363014	42.9999
0.680000	0.101291	0.00764811	0.367873	48.0999
0.670000	0.0908357	0.00690919	0.372712	53.9443
0.660000	0.0811650	0.00622292	0.377531	60.6679
0.650000	0.0722472	0.00558689	0.382335	68.4344
0.640000	0.0640507	0.00499877	0.387126	77.4444
0.630000	0.0565431	0.00445631	0.391906	87.9441
0.620000	0.0496920	0.00395735	0.396678	100.238
0.610000	0.0434642	0.00349975	0.401443	114.706

T_r	P_r	η_g	η_l	$r=\eta_l/\eta_g$
0.600000	0.0378266	0.00308146	0.406204	131.822
0.590000	0.0327457	0.00270043	0.410964	152.185
0.580000	0.0281880	0.00235466	0.415724	176.553
0.570000	0.0241202	0.00204219	0.420487	205.899
0.560000	0.0205089	0.00176108	0.425254	241.474
0.550000	0.0173212	0.00150938	0.430028	284.903
0.540000	0.0145244	0.00128522	0.434812	338.317
0.530000	0.0120866	0.00108670	0.439606	404.534
0.520000	0.00997654	0.000911963	0.444414	487.316
0.510000	0.00816368	0.000759187	0.449237	591.734
0.500000	0.00661863	0.000626568	0.454078	724.708
0.490000	0.00531310	0.000512340	0.458940	895.772
0.480000	0.00422011	0.000414780	0.463823	1118.24
0.470000	0.00331411	0.000332215	0.468731	1410.93
0.460000	0.00257110	0.000263031	0.473666	1800.80
0.450000	0.00196873	0.000205679	0.478631	2327.08
0.440000	0.00148643	0.000158688	0.483629	3047.67
0.430000	0.00110540	0.000120671	0.488661	4049.54
0.420000	0.000808726	0.0000903340	0.493730	5465.61
0.410000	0.000581324	0.0000664862	0.498841	7502.93
0.400000	0.000409965	0.0000480421	0.503995	10490.7

The reduced temperature and pressure of the pure hard core fluid are T_r and P_r respectively. η_g and η_l are the reduced densities of the gas and liquid phases at coexistence.

