

PHASE EQUILIBRIA AND CRITICAL PHENOMENA
IN SIMPLE FLUID SYSTEMS

by

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To the memory of my mother

ABSTRACT

The penetrable-sphere models of liquid vapour equilibrium are a class of one-component continuum models in which molecules interact with multibody potentials. They are isomorphic with binary mixtures where the interactions are simple pair potentials. Both versions exhibit phase separation and critical points.

The properties of the multibody potentials of the one-component model are studied and the equivalence of this with the two-component model is demonstrated; a set of transcription rules is obtained and used to transcribe the distribution functions. A simple relation is found between the one- and two-component direct correlation functions which is exploited in the mean-field approximation (MFA). The critical behaviour of the correlation functions is studied in detail in this approximation.

The binary mixture is extended to a three-component system and the phase separation is investigated in the MFA and also with a six-term virial series. Two phase transitions of interest are discussed, the one continuous and the other discontinuous. The former corresponds to the simultaneous vanishing of three phases in a tricritical point; the latter corresponds to four-phase equilibrium. The vanishing of the order parameters at the tricritical point is represented by exponent laws and the values of the exponents are obtained. From these values, it is proposed that the tricritical point is classical.

The critical point in the binary mixture model and in a more realistic system, namely one where molecules interact with Lennard-Jones potentials, are investigated with the Percus-Yevick (PY) and hypernetted chain (HNC) integral equations. In the first model, Padé approximants are used to obtain the singular behaviour of the truncated virial series; in the Lennard-Jones fluid the integral equations are solved numerically. It is concluded that the two integral equations predict critical points of different nature. The PY is classical in both models; the HNC is non-classical and realistic in the penetrable-sphere model and non-classical but unrealistic in the Lennard-Jones fluid.

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Chapter I

INTRODUCTION

I.1 The theories of Van der Waals and Landau

The study of critical points began just over one hundred years ago when Thomas Andrews of Queen's College, Belfast, carried out, during 1861 to 1869, a series of experiments on the liquefaction of several gases. In the Bakerian lecture published in June 1869 in the Philosophical Transactions of the Royal Society he reported his discovery of a striking "continuity of the gaseous and liquid states of matter". Six years earlier he had observed that above 88°F (31°C) no distinction between gaseous and liquid carbon dioxide was possible. In his words [1]:

On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to 88°F, the surface of demarcation between the liquid and gas became fainter, lost its curvature and at last disappeared. The space was then occupied by a homogeneous fluid which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striae throughout its entire mass. At temperature above 88°F no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results.

In the following experiments he measured the CO₂ isotherms and determined precisely the "critical point". He concluded that [1]:

The ordinary gaseous and liquid states are only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity.

Some work had been done before, mainly by van Marum of Haarlem in the eighteenth century and Caignard de la Tour of Paris in 1822 but no one had observed such a striking continuity of phases.

Just three years later, in June 1873, Johannes Diderik van der Waals gave a theoretical explanation of Andrews's experiment. In his thesis whose title is a translation of the Bakerian lecture [2, 3] he proposed an equation of state, based on the new kinetic theory, which takes into account the passage from the gas to the liquid state. He proposed

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad (1-1)$$

where the first term he interpreted as a correction to the pressure due to the attractive nature of intermolecular forces. Using Clausius's

virial theorem and the assumption that the range of intermolecular forces is long compared with the mean free path, he was able to demonstrate that the reduction in pressure is proportional to the square of density. The finite size of the molecules, i.e. the repulsive core of the forces lead in a somewhat empirical argument to the second term.

Recognition came very rapidly, first in Britain then elsewhere [3]. Van der Waals gave a remarkably good qualitative description of gas-liquid phase transition. His equation is cubic in density and so has three roots for a given pressure and temperature. Above a critical temperature, T_c , there is only one real root representing the supercritical fluid and below T_c there are three roots corresponding to the two-phase region. The equation thus reproduces the continuity of the gaseous and liquid phases and their critical point discovered by Andrews. Figure 1 shows the p - V phase diagram of a fluid obeying Van der Waals equation of state,

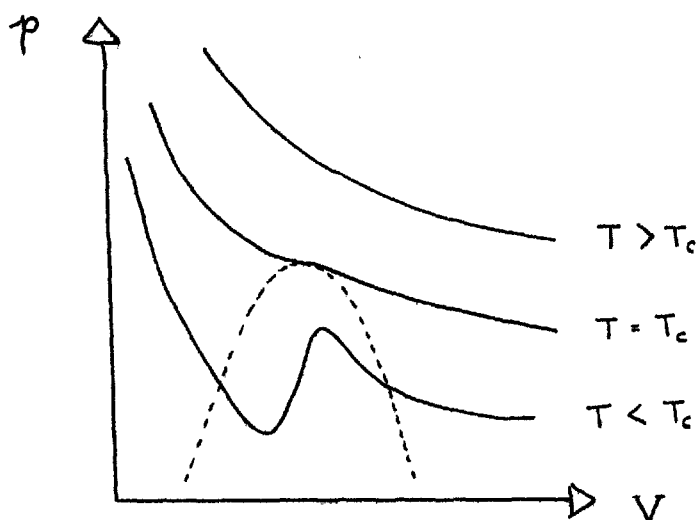


Fig. 1. Phase diagram of a fluid obeying Van der Waals's equation of state.

A drawback, however, is that the isotherms exhibit a wholly unstable portion in the two-phase region where the compressibility is negative. A later (1875) suggestion by Maxwell showed how to overcome this unpleasant feature [4]. His proposal known as the equal-area rule enables one to obtain the saturated volumes and vapour pressure, p_g , from the sigmoid isotherms: the line $p=p_g$ is drawn to cut the loops in two areas of equal size.

Van der Waals's equation is a remarkable achievement of the application of microscopic concepts to explain macroscopic phenomena. However it failed to reproduce accurately experimental phase transitions particularly in the vicinity of the critical point. It is known now that the disagreement reflects a tacit assumption of infinitely long ranged forces. In fact, Boltzmann pointed out that a long ranged force would be necessary to "obtain an exact foundation" for that equation of state, to which Van der Waals replied that he never had made such assumption and that it should be physically impossible [5]. In 1963 Kac, Uhlenbeck and Hemmer [6] demonstrated that a one-dimensional fluid whose molecules interact in pairs with a potential $\psi(x)$ which consists of a hard core and an exponential attraction $\psi_{\text{attr}}(x)$ (fig. 2) undergoes a phase transition on the limit of the force becoming infinitely weak and infinitely long ranged so that the integral

$$\int_0^{\infty} \psi_{\text{attr}}(x) dx \quad (1-2)$$

remains finite. The phase transition is described exactly by the Van der Waals equation but with a flat portion to the isotherms.

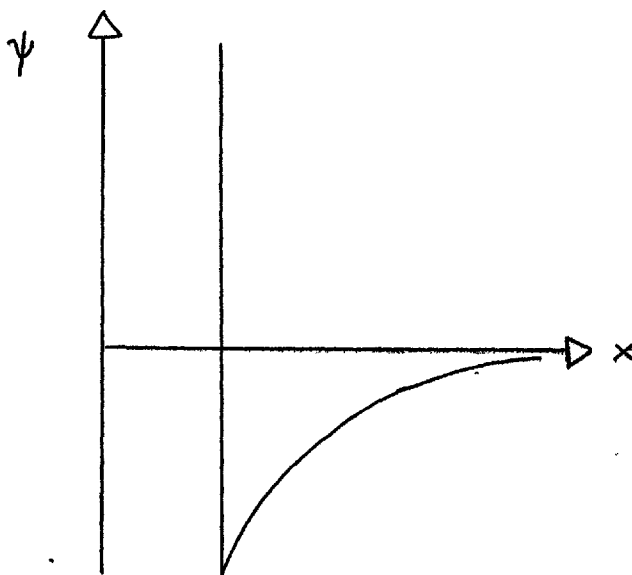


Fig. 2. Kac potential.

In terms of molecular interactions the fundamental assumption of Van der Waals is that the "internal pressure", i.e. that which reduces

the external pressure, is caused by some smeared interaction exerted upon each molecule by the rest. This idea was expressed very clearly by Pierre Weiss in his theory of ferromagnetism [7]:

I assume that each molecule experiences an action of the rest of the ensemble equal to a uniform field proportional to the magnetization and in the same direction of it. I propose the name of internal field in analogy to the internal pressure of Van der Waals. (p. 602)

The concept of a "mean field" has been very fruitful since then. It may be introduced in a number of equivalent ways:

- i) Molecules occupying random positions interact as a uniform field.
- ii) An effectively constant field implies that there are no density fluctuations.
- iii) The effect of a uniform field can be produced by an infinite number of nearest neighbours, hence the mean field approximation is expected to be exact in a system of infinite dimensionality.
- iv) As Boltzmann pointed out [5] and Kac, Uhlenbeck and Hemmer [6] later demonstrated, an infinitely-weak, infinitely long-ranged potential produces the effect of a mean field.
- v) In terms of thermodynamic functions, the mean field description of critical phenomena is equivalent to assuming that the relevant thermodynamic potential may be expanded about the critical point in Taylor series [8]; therefore only even powers of the independent variables are included (odd powers vanish by symmetry).

The latter point is what constitutes the basis of Landau's theory of critical phenomena [9]. The critical point is a unique (p_c, V_c) point on the $A(p, V)$ surface determined by the two conditions:

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^3 A}{\partial V^3}\right)_T = 0$$

or equivalently

(1-3)

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

The consequences of those conditions were first investigated by Van der Waals himself [10] in 1894 and in more detail by Verschaffelt [11] in 1907 but are commonly ascribed to Landau because of the elegant treatment he developed later.

Landau's approach is particularly useful in the light of modern theories of critical exponents as he brings out the dominant behaviour

of the thermodynamic quantities near the critical point. The essential steps of this theory are the following [12]:

1. An appropriate set of thermodynamic variables, such as $T-T_c$ or $\rho-\rho_c$, is chosen. They become zero at the critical point and represent a certain "order parameter" whose vanishing characterizes the disappearance of any distinction between the coexisting phases. An appropriate free energy, function of those variables, is selected.
2. The free energy is expanded in powers of $\rho-\rho_c$ at constant T with coefficient $a_n(T)$.
3. The coefficients in turn are expanded in powers of $T-T_c$ with the assumption that the leading coefficient vanishes to yield an infinite compressibility at the critical point.
4. A minimization of the free energy is involved in order to remove the sigmoid loops of the isotherm below T_c .

Some of those points are open to criticism [12]. 2 for example is expected to be valid above T_c but it is dubious at and below T_c ; 3 is unjustified, particularly for $T < T_c$ as it leads to unstable and metastable portions of the isotherms just as the Van der Waals equation does. Those instabilities are removed by 4 but this is an ad hoc assumption and furthermore it is inconsistent with a rigorous stability treatment. Nonetheless Landau's theory succeeds in exhibiting the critical behaviour of thermodynamic quantities as power laws and produces explicit values of the critical exponents.

1.2 The Ornstein - Zernike theory of critical scattering

A different approach was taken by Ornstein and Zernike in 1914. They focused their description on a microscopic theory of critical fluctuations but their predictions are essentially equivalent to those of the mean-field theories, i.e. they are also classical. It had been known for some time that fluids exhibit a very sharp increase in the forward light scattering near their critical points. Those were the "moving or flickering striae" observed by Andrews heralding the vanishing of the surface of demarcation between the liquid and the gaseous phases. Smoluchowski [13] in 1908 ascribed that critical opalescence to the increase of (independent) local fluctuations and Einstein [14] developed a theory of critical scattering based on the assumption of statistically independent fluctuations. However their theory could not account for the asymmetry in the direction of scattering (most of the increase is in the forward direction) which is the distinctive feature of critical opalescence. It was not until four years later that Ornstein and Zernike

[15] recognized that the correlation of density fluctuations, roughly true away from the critical region, was no longer a valid assumption [16].

The Ornstein-Zernike (OZ) theory rests upon the concept of a correlation function, defined below through equations (1-9) to (1-11). Intuitively, they are a measure of the structure of the fluid, that is, the correlation functions are proportional to the probability that a density fluctuation in a microscopic element of volume induces a density fluctuation in some other element of volume separated by a distance r . When the critical point is approached the fluid begins to act collectively; density fluctuations induce other fluctuations at distances so large compared with the size of the molecules that one may rightfully speak of an infinitely long correlated system. In practice the "correlation length", i.e. the average distance of a correlation, becomes of the order of magnitude of the wavelength of visible light and therefore it is observed a considerable increase of light scattering from the critical fluid.

In the OZ theory those critical fluctuations are accounted by two functions called the total and the direct correlation functions. They are related to distant-neighbour and nearest-neighbour fluctuations respectively. The total correlation function increases characteristically its range as the system becomes critical while the direct correlation function is short-ranged at every temperature, including the critical. The two functions are connected by an integral equation ((1-6) below) whose meaning is shown schematically in Figure 3. Correlations between two distant elements of volume, 1 and n , are "transmitted" via nearest-neighbour (direct) correlations, j to $j+1$. It is clear then how long-range order is attained with only short-ranged correlations. Near the critical point macroscopic regions of the system are so correlated that they act as single units.

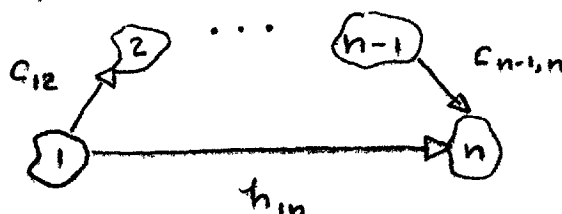


Fig. 3. Direct and total correlation functions in the Ornstein-Zernike theory.

We may conveniently define $c(r)$ in terms of $h(r)$ in Fourier space. Let $\tilde{h}(k)$ be the Fourier transform of the total correlation function $h(r)$ and $\tilde{c}(k)$ that of the direct correlation function $c(r)$. According to the OZ theory they are related by

$$\begin{aligned} 1 + n \tilde{h}(k) &= \frac{1}{1 - n \tilde{c}(k)} \\ &= 1 + n \tilde{c}(k) + n^2 [\tilde{c}(k)]^2 + \dots \end{aligned} \quad (1-4)$$

where $n=N/V$ is the number density. Actually (1-4) is only a definition of $\tilde{c}(k)$ in terms of $\tilde{h}(k)$ (or vice versa) as it renders no information on the form of either. This has to be supplied by an additional hypothesis. For the moment we observe that (1-4) indeed contains the physical properties ascribed to c , in fact $\tilde{c}(k)$ is little affected by temperature (the same can be said for $c(r)$) since

$$\begin{aligned} \tilde{c}(k) &\approx n \tilde{h}(k) & \text{for} & & n \tilde{h}(k) \ll 1 & \text{(high } T) \\ \tilde{c}(k) &= \frac{1}{2} n \tilde{h}(k) & \text{for} & & n \tilde{h}(k) = 1 & \\ \text{and } \tilde{c}(k) &\rightarrow 1 & \text{for} & & n \tilde{h}(k) \rightarrow \infty & (T \rightarrow T_c) \end{aligned} \quad (1-5)$$

Fourier inversion of (1-4) leads to the OZ integral equation

$$h(\underline{r}) = c(\underline{r}) + n \int c(\underline{r} - \underline{r}') h(\underline{r}') d\underline{r}' \quad (1-6)$$

The physical significance of $h(\underline{r})$ and $c(\underline{r})$ can be made more transparent from (1-6) by the successive substitution of $h(\underline{r})$ into the integrand to give [17]

$$\begin{aligned} h(\underline{r}) &= c(\underline{r}) + n \int c(\underline{r} - \underline{r}') c(\underline{r}') d\underline{r}' + \\ &+ n^2 \iint c(\underline{r} - \underline{r}') c(\underline{r}' - \underline{r}'') c(\underline{r}'') d\underline{r}' d\underline{r}'' + \dots \end{aligned} \quad (1-7)$$

that is, the total correlation is made of two parts, one expressing the direct correlation between neighbouring molecules ($c(r)$), and the other dealing with the "propagation" of correlation. It is in this way that infinitely long-ranged correlations are established when macroscopic regions of the system become correlated in the vicinity of the critical point.

The relation with Thermodynamics is established by fluctuation theory. The fluctuations in the total number of particles are given in the grand canonical ensemble by [18]

$$\langle (N - \langle N \rangle)^2 \rangle = n^2 k T V K_T \quad (1-8)$$

where K_T is the isothermal compressibility. These fluctuations can also be calculated from the m -body distribution function defined by

$$n^{(m)}(\underline{r}_1, \dots, \underline{r}_m) = \Xi^{-1} \sum_{N \geq m} \frac{1}{h} \frac{N!}{3N N!} \frac{N!}{(N-m)!} \iint d\underline{r}_{m+1} \dots d\underline{r}_N \exp(-\beta H_N + \beta \mu N) \quad (1-9)$$

where Ξ is the grand partition function. $n^{(m)}$ is a measure of the conditional probability of having m particles distributed into a given configuration $\underline{r}_1, \underline{r}_2, \dots, \underline{r}_m$. The total correlation function is defined as a convenient normalization of the two-body distribution function. To this end we define an auxiliary function, called the pair correlation function, which in a uniform fluid is given by [16]

$$g(\underline{r}, \underline{r}') = \frac{n^{(2)}(\underline{r}, \underline{r}')}{n^{(1)}(\underline{r}) n^{(1)}(\underline{r}')} = \frac{n^{(2)}(\underline{r}, \underline{r}')}{n^2} \quad (1-10)$$

When the system is in a single phase, $g(r) \rightarrow 1$ as $r \rightarrow \infty$. The total correlation function, $h(r)$, is defined as the difference between $g(r)$ and its random value, that is

$$h(r) = g(r) - 1 \quad (1-11)$$

Hence $h(r)$ decays to zero as $r \rightarrow \infty$.

The fluctuations in the total number of particles is found by integrating (1-9) for $m=1$ and $m=2$ and substituting the definition of $h(r)$, eq. (1-11). Combining this result with (1-8) there is obtained the compressibility equation relating K_T to $h(r)$ by [16]

$$n k T K_T = 1 + n \int h(\underline{r}) d\underline{r} \quad (1-12)$$

Equation (1-12) is the mathematical statement of the observation that $h(r)$ becomes infinitely long ranged at the critical point. As the integral of $h(r)$ must be a bounded function over a finite region because of

the incompressibility of real molecules, eq. (1-12) is consistent with the divergence of the compressibility only if $h(r)$ itself becomes infinitely long ranged at the upper limit.

The basic framework of the theory is thus established, but we are still without an expression for $c(r)$ or, equivalently, for $h(r)$. Fortunately $h(r)$ or, rather, its Fourier transform, is accessible to experimental determination. Let $I(\underline{k})$ be the scattering intensity of some electromagnetic radiation (or sometimes thermal neutrons) incident upon a sample of fluid in the direction $\underline{k}=0$ and scattered at an angle θ . Neglecting multiple scattering we have the relation [16]

$$I(\underline{k})/I_0(\underline{k}) \equiv S(\underline{k}) = 1 + n \tilde{h}(\underline{k}) \quad (1-13)$$

where $I_0(\underline{k})$ is the scattering intensity in the absence of correlations. $S(\underline{k})$ is called the structure factor and measures the response of the fluid to an imposed periodical perturbation of wave number $\underline{k}$ [19]. Comparison of (1-13) with (1-12) shows that

$$\begin{aligned} S(0) &= \lim_{\underline{k} \rightarrow 0} \frac{I(\underline{k})}{I_0(\underline{k})} = 1 + n \tilde{h}(0) \\ &= nkT K_T \end{aligned} \quad (1-14)$$

so the increase in forward scattering in the critical region, measured by $S(0)$, is a consequence of the divergence of the compressibility at the critical point. From (1-4) we also can relate $S(0)$ to $\tilde{c}(0)$ as

$$1 + n \tilde{h}(0) = (1 - n \tilde{c}(0))^{-1} \quad (1-15)$$

and consequently

$$S^{-1}(0) = 1 - n \tilde{c}(0) \quad (1-16)$$

Equation (1-16) means that $1 - n \tilde{c}(0) = 0$ at the critical point, that is $\int c(\underline{r}) d\underline{r} = 1$ and thus the integral of $c(r)$ indeed remains finite.

At this stage Ornstein and Zernicke introduced the assumption that $\tilde{h}(\underline{k})$ is holomorphic in some neighbourhood of the real axis. On the positive real axis this function can only have a pole at the origin when $T = T_c$. It follows from (1-15) that $\tilde{c}(\underline{k})$ is also holomorphic in the same neighbourhood and hence admits a Taylor expansion about $\underline{k} = 0$. They

further assumed that $c(r)$ is short-ranged enough so the expansion of $\tilde{c}(k)$ can be truncated after the first term (in k^2), and that the second moment of $c(\underline{r})$

$$R^2 = \frac{1}{2n} \langle \cos^2 \theta \rangle \int r^2 c(\underline{r}) d\underline{r} \quad (1-17)$$

remains finite at the critical point. The expansion of $S(k)$ near $k = 0$ is, under these conditions

$$S(k) \approx \frac{R^{-2}}{\kappa^2 + k^2}, \quad k^2 \rightarrow 0 \quad (1-18)$$

where κ has the units of inverse length and is defined by

$$\kappa^2 = \frac{(1 - n\tilde{c}(0))}{R^2} \quad (1-19)$$

Fourier inversion of (1-18) yields, in three dimensions

$$h(r) \approx \frac{1}{4\pi n R^2} \frac{\exp(-\kappa r)}{r} \quad \begin{array}{l} r \rightarrow \infty \\ T \rightarrow T_c \end{array} \quad (1-20)$$

1-16, and 1-19

By (1-14), though, we have that

$$K_T = (kTnR^2\kappa^2)^{-1} \quad \begin{array}{l} r \rightarrow \infty \\ T \rightarrow T_c \end{array} \quad (1-21)$$

thus

$$\kappa(T) \rightarrow 0 \quad \text{as} \quad T \rightarrow T_c \quad (1-22)$$

hence

$$h(r) \approx \frac{D}{r} \quad \begin{array}{l} r \rightarrow \infty \\ T = T_c \end{array} \quad (1-23)$$

so, at the critical point, $h(r)$ is no longer exponentially damped but decays to zero as r^{-1} .

Equation (1-18) has two main experimental predictions: (a) that

graphs of $S^{-1}(k)$ against k^2 should be straight lines and (b) the extrapolated intercepts with the axis $k^2 = 0$ should be proportional to $K_T^{-1}(T)$ (eq. (1-14)) and therefore go to zero as $T \rightarrow T_c$. Careful measurements have verified (b) but the linear variation of $S^{-1}(k)$ with k^2 is true only for larger values of k^2 and the lines show a slight curvature downwards for small values of k^2 (Figure 4).

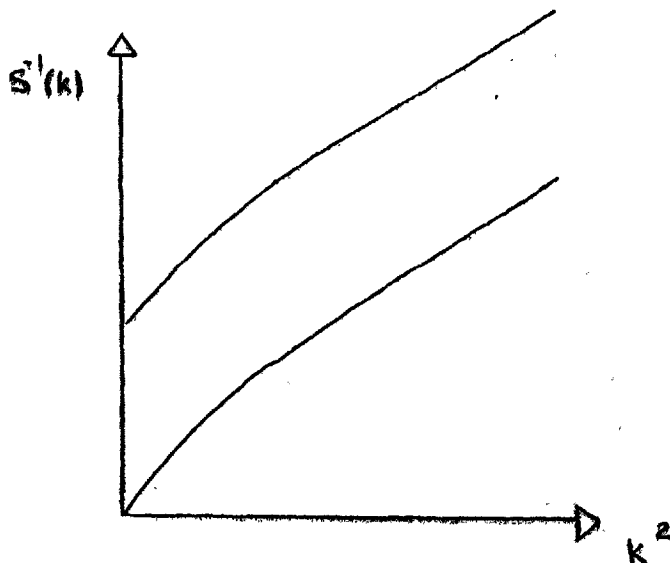


Fig. 4. Observed dependence of $S^{-1}(k)$ on k^2 near the critical point (schematic).

This slight curvature has important repercussions on the validity of the OZ theory. As Fisher [16] has pointed out, $h(r)$ decays at the critical point of a d -dimensional system as

$$h(r) \approx \frac{D}{r^{d-2+\eta}} \quad (1-24)$$

where the index η ($0 \leq \eta < 2$) measures the departure from the OZ theory. The important point is that (1-24) implies that

$$c(r) \sim r^{-(d+2-\eta)} \quad (1-25)$$

that is, when $\eta > 0$, $c(r)$ is also weakly long-ranged and so its second moment diverges at the critical point (although the first moment still converges because of (1-16)). Recent measurements have verified that η , though small, is indeed greater than zero.

I.3 The order parameter and critical exponents

The modern theory of critical points aims to understand the nature of the singularity in terms of the divergence of thermodynamic or statistical quantities. The central point of the theory is to characterize such divergences in terms of power laws which relate the way in which an "order parameter" disappears as the appropriate thermodynamic variable assumes its critical value.

We have already encountered the idea of an order parameter in Landau's theory. It is a measure of the proximity to the point where a physical quantity goes to zero. Thus in a liquid-vapour critical point the order parameter may be the difference between the densities of the liquid and vapour phases as the critical point is approached from the two-phase region.

The critical exponent characterizes the asymptotic behaviour of a function $f(\epsilon)$ when the order parameter ϵ tends to zero. It is formally defined by [12]

$$\lambda = \lim_{\epsilon \rightarrow 0} \frac{\log f(\epsilon)}{\log \epsilon} \quad (1-26)$$

assuming that $f(\epsilon)$ is positive and continuous for sufficiently small values of ϵ . It is customary to express the relation (1-26) in the shorthand notation

$$f(\epsilon) \sim \epsilon^\lambda \quad (1-27)$$

This equation does not imply that $f(\epsilon) = A\epsilon^\lambda$ at all ϵ , because some correction terms are always present. There may be two cases [12]. In a simple one the correction is accounted by a polynomial,

$$f(\epsilon) = A \epsilon^\lambda (1 + B \epsilon^\mu + \dots) \quad (\mu > 0) \quad (1-28)$$

which does not conceal the asymptotic behaviour as $\epsilon \rightarrow 0$. The critical exponent is obtained from log-log plots of $f(\epsilon)$ against ϵ where λ is the limiting slope. But there may be a non-simple case where logarithmic factors such as

$$f(\epsilon) = A |\log \epsilon|^\mu \epsilon^\lambda (1 + B \epsilon^\nu + \dots) \quad (1-29)$$

arise. In such cases, determination of λ may be very difficult or even impossible without full information on higher order terms. The case $\lambda = 0$ is ambiguous. Normally it is ascribed to a logarithmic divergence (in the simple case)

$$f(\epsilon) = A \log \epsilon + B + \dots \quad (1-30)$$

although other possibilities such as a finite discontinuity are equally consistent with (1-26).

The four most usual critical exponents involving only thermodynamic variables are denoted by α , β , γ , and δ . They relate the divergences of the heat capacity at constant volume and the compressibility and the shapes of the coexistence curve and the critical isotherm in the critical region. The specific heat at constant volume, C_V , has been observed to increase sharply near T_c and it is usually regarded as diverging logarithmically. We write

$$\begin{aligned} C_V(\rho = \rho_c, T) &\sim (T - T_c)^{-\alpha} \quad (T > T_c) \\ &\sim (T_c - T)^{-\alpha'} \quad (T < T_c) \end{aligned} \quad (1-31)$$

(primed exponents indicate that the critical point is approached from below T_c). The shape of the coexistence curve is defined in terms of the way the order parameter $\rho_l - \rho_g$ vanishes. We define the corresponding exponent by

$$\rho_l - \rho_g \sim (T_c - T)^\beta \quad (T < T_c) \quad (1-32)$$

The approach to the critical point from within the one-phase region is most commonly characterized by the divergence of the isothermal compressibility, which along the critical isochore $\rho = \rho_c$ behaves as

$$K_T(\rho = \rho_c, T) \sim (T - T_c)^{-\gamma} \quad (1-33)$$

Since K_T becomes infinite at the critical point, the critical isotherm must have a horizontal tangent there. Its shape is described by

$$p - p_c \sim \text{sgn}(\rho - \rho_c) |\rho - \rho_c|^\delta \quad (1-34)$$

The critical indices must be defined along a specified path. In some cases the indices defined along several paths coincide (as in the case of $\gamma'_l = \gamma'_g = \gamma'$ relating the exponents of the compressibility along the condensation and boiling lines of the two-phase region) but this is not necessarily always the case [12].

There are several reasons for devoting such importance to the critical indices. In the first place it is an experimental fact that thermodynamic functions become zero or infinite according to (1-27). The critical exponent is accessible to measurement while the complete functional form (1-28) or (1-29) is usually not. Secondly there are a number of inequalities derived on the grounds of thermodynamic stability which the critical indices must obey. The two most important involving only the exponents of thermodynamic functions are [8]

$$\alpha' + 2\beta + \gamma' \geq 2 \quad (1-35)$$

$$\alpha' + \beta(1 + \delta) \geq 2 \quad (1-36)$$

More thermodynamic inequalities in fluid and magnetic systems were subsequently derived, many of them by Griffiths [20]. A comprehensive list of inequalities may be found in his paper.

Two more critical indices, η and ν , related to the correlation functions are commonly used. We have already defined the exponent η which appears in Fisher's correction to the OZ theory. The inverse correlation length, $\kappa(T)$, introduced in (1-18), becomes zero at the critical point as

$$\kappa(T) \sim |T - T_c|^\nu \quad T \rightarrow T_c \quad (1-37)$$

These indices are related to γ by the equality [16]

$$\gamma = (2 - \eta)\nu \quad (1-38)$$

It is important to underline that these relations follow from general arguments and do not depend in any way on the Hamiltonian.

Recently Widom [21], Kadanoff [22] and others [23] have put forward the "scaling hypothesis" where a very general equation of state is proposed and which is presumed to be valid in the neighbourhood of the

critical point irrespective of the details of the Hamiltonian. One of its consequences is that the inequalities among the critical indices (1-35), (1-36), (1-38) become equalities leaving only two independent indices. The verification of the scaling hypothesis has become an important task in the study of critical phenomena.

One important point that has emerged from the study of critical exponents is the inadequacy of mean-field theories to reproduce quantitatively the experimental behaviour. Some time ago Guggenheim [24] showed that the law of corresponding states was obeyed by the gases Ne, Ar, Kr, Xe, N₂, O₂, CO and CH₄, with $\beta = \frac{1}{2}$ rather than $\beta = \frac{1}{4}$. Later measurements and model studies have completed the list of "real" critical exponents which all differ from their classical values. Some of the critical exponents are listed in Table I.

I.4 The Lenz - Ising model

A more realistic insight into critical phenomena has been obtained by the study of model systems, of which the Lenz-Ising model has been the most widely employed.

The model was suggested by Lenz to his student Ising as being applicable to an elementary ferromagnet. It considers a regular crystal lattice in which a spin, assigned to each site, can align parallel or antiparallel to an externally imposed magnetic field. The interaction energy between neighbouring spins is $+J$ if they are antiparallel and $-J$ if they are parallel ($J > 0$). Ising was able to solve the one-dimensional lattice [25] but to his disappointment no phase transition was shown for any temperature other than $T = 0$. In 1936, however, Peierls [26] demonstrated rigorously that the two- and three-dimensional models undergo a phase change. (His argument had an incorrect step which was later corrected by Griffiths [27]). Peierls drew closed contours enclosing regions of only parallel or only antiparallel spins and established a biunivocal correspondence between contours and spin configurations. Next he demonstrated that below a critical (non-zero) temperature the area or volume enclosed by the contours surrounding only antiparallel spins was only a small fraction of the total area or volume and therefore that most of the spins would be parallel, leading to a net magnetization. Eight years later, in 1944, Onsager [28] published his analytical solution to the planar lattice in zero external field. The results are completely different from the classical theories. A logarithmic divergence of the heat capacity was found, both above and below T_c , instead of a finite discontinuity, and the magnetization approached zero with a one-eighth-power

Exponent	Definition	Experimental value* (CO ₂)	Classical theory	Ising model (d = 2)	Ising model (d = 3)
Below T _c	At coexistence T → T _c				
α'	C _V ~ ΔT ^{-α'}	0.1	0 (discont.)	0 (log)	$\frac{1}{16} \pm 0.16$ $\frac{1}{16} - 0.035$
β	ρ _l - ρ _g ~ ΔT ^β	0.34	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{5}{16} \pm 0.003$ $\frac{5}{16} - 0.006$
γ'	K _T ~ ΔT ^{-γ'}	1.26 ± 0.02**	1	$\frac{7}{4}$	$\frac{21}{16} \pm 0.03$ $\frac{21}{16} - 0.05$
ν'	κ(T) ~ ΔT ^{ν'}		$\frac{1}{2}$	1	$\left(0.675 \pm 0.02\right)$ $\left(0.675 - 0.03\right)$
At T = T _c	ρ → ρ _c				
δ	p - p _c ~ ρ - ρ _c ^δ	4.2	3	15	$\frac{26}{5} \pm 0.15$
η	I(k)/I ₀ (k) ~ k ^{-(2-η)}		0	$\frac{1}{4}$	$\frac{1}{18} \pm 0.008$
Above T _c	ρ = ρ _c , T → T _c ⁺				
α	C _V ~ ΔT ^{-α}	0.1	0 (discont.)	0 (log)	$\frac{1}{8} \pm 0.015$
γ	K _T ~ ΔT ^{-γ}	1.26 ± 0.02**	1	$\frac{7}{4}$	$\frac{5}{4} \pm 0.003$
ν	κ(T) ~ ΔT ^{-ν}	0.6	$\frac{1}{2}$	1	$\frac{9}{14} \pm 0.0025$

Table I. Critical exponents in some theories.
(ΔT ≡ |T - T_c|) from ref. [12].

* Ref. [23]. ** M. Vincentini-Missoni, J.M.H. Levelt-Sengers and M.S. Green (1969) J. Res. NBS 73A, 563.

law. The pair correlation function showed the most interesting result as it is of the form [29]

$$g(r) \approx r^{-\frac{1}{4}} \exp \left[-Br \left(\frac{T}{T_c} - 1 \right) \right] \quad (T \gtrsim T_c) \quad (1-39)$$

instead of

$$g(r) \approx (\log r) \exp \left[-B'r \left(\frac{T}{T_c} - 1 \right)^{\frac{1}{2}} \right] \quad (T \gtrsim T_c) \quad (1-40)$$

which results from inverting (1-18) (OZ theory) for $d = 2$ and is clearly nonsense.

Onsager's exact solution rests on two symmetry properties of the model. The first, common to all dimensionalities, is the symmetry between parallel and antiparallel spins. If all spins are inverted the interaction energy remains unchanged. This leads to a one-to-one correspondence of states with positive and negative magnetization. The second property is exclusive to two-dimensional lattices and depends on the concept of a dual lattice, which is constructed in such a way that the sites of that lattice are situated on the centres of the original lattice and vice versa. This leads to a one-to-one correspondence for pairs of states at T_c above and below T_c at zero field. No such property has been found for the three-dimensional lattice and hence Onsager's solution to the planar lattice remains one of the few exact treatments of phase transitions. However many numerical studies have characterized well the three dimensional lattice.

Although the Lenz-Ising model was proposed for magnetic phase transitions an extension has been made to the study of liquid-vapour equilibrium. In 1952 Lee and Yang [30] extended the ideas so far applied to the Lenz-Ising model to an hypothetical fluid called the lattice gas. In this system the space is divided in a number of "boxes" of such size that they can be either occupied or vacant. The hole-particle symmetry was found to be entirely equivalent to the parallel-antiparallel spins and much of what was later derived was based on this fact. An unattractive feature of the model is that the potential depends on a rather artificial confinement of the particles to preassigned sites. This can be roughly adequate for a crystal but it is certainly untrue in a fluid.

An interesting generalization of the Lenz-Ising model in another direction was developed by Potts [31] in 1952. He considered a two dimensional lattice as in the ordinary Lenz-Ising model but allowed each spin to be in q different states. Neighbouring spins interact with different

energies according to whether they are in the same or different states. Naturally the Lenz-Ising model corresponds to $q = 2$. The three-state model ($q = 3$) has aroused much interest recently for its connection with tricritical phenomena (i.e. three phases vanish simultaneously). In this case neighbouring sites interact with energy ϵ_0 if they are in the same state and ϵ_1 if they are in a different state. In the ferromagnetic case $\epsilon_0 < \epsilon_1$. The system shows a continuous (higher order) phase transition where all three phases vanish in a tricritical point. Straley and Fisher [32] exhibited that point by series analysis and remarked that it was an "anomalous" tricritical point in the sense that all three phases come to vanish on equal footing while in a "normal" tricritical point they do not [33]. We will return to this point later in connection with a continuous model of ternary equilibria but we will consider first another important generalization of lattice models.

1.5 The penetrable-sphere model

In 1970 Widom and Rowlinson [34] proposed an alternative model to the lattice gas, having an underlying symmetry closely analogous (but not strictly identical) to the hole-particle symmetry but with the realistic feature of being a true continuum model, and thus being more adequate for the study of liquid-vapour equilibrium. In the new model a multibody potential energy was defined for a one-component system as a function of the total volume covered by N microscopic spheres (in general interpenetrating, hence the name) each centred on one molecule and having constant volume v_0 . If $W(\underline{r}_1, \dots, \underline{r}_N)$ represents the common volume of the N interpenetrating spheres, the potential energy is given by [34]

$$U(\underline{r}_1, \dots, \underline{r}_N) = - \frac{\epsilon}{v_0} [Nv_0 - W(\underline{r}_1, \dots, \underline{r}_N)] \quad (1-41)$$

where ϵ is a microscopic parameter with units of energy. This one-component fluid was demonstrated to be isomorphic to a binary mixture in which the particles interact with purely pair potentials in which molecules of the same species see each other as ideal gases but those of different species interact as hard spheres. The thermodynamic properties of one "version" are transcribed into the other by simple rules derived in the process of demonstrating their equivalence. The symmetry becomes more apparent in the two component version where both species play identical roles.

Because of the interactions proposed, the mixture is expected to segregate into two phases, each consisting mostly of one species, when the density of both is high. This separation cannot persist at low densities because of the entropic contribution to the free energy and thus a critical point (plait point) is expected at some intermediate density. Widom and Rowlinson exploiting the symmetry of the model were able to locate the critical point by a number of inequalities and characterize some of the asymptotic behaviour of thermodynamic variables. One interesting consequence of this model is that the mean orthobaric density of the one-component version (which coincides with the line of symmetry in the two-phase region) reflects the singularity of the heat capacity so that the law of rectilinear diameters fails. This failure is associated with the deviation from the strict hole-particle symmetry of the lattice gas [35]. Though it has not been shown beyond doubt it seems that experimental systems have singular diameters.

The model was shown to be correct in the limits of low and high temperatures. In the first one it is correct because it has the right symmetry, in the second one it gives rise to the mean field approximation. In fact, one of the equivalent formulations of this approximation is that of molecules occupying random positions; the mean volume $\langle W \rangle$ covered by the N interpenetrating spheres is simply, in the thermodynamic limit.

$$\frac{\langle W \rangle}{V} = 1 - \exp(-\rho) \quad (1-42)$$

where $\rho = v_0 N/V$ is a dimensionless density. From (1-41) it follows that the potential energy density of the random configuration is

$$\phi = 1 - \rho - \exp(-\rho) \quad (1-43)$$

where $\phi = v_0 \bar{U}/\epsilon V$. Thermodynamic properties follow from this equation of state.

Further developments followed rapidly. Ruelle [36] using a modified version of Peierls's argument proved the existence of a phase transition for the mixture model in two dimensions (and by implication in higher dimensionalities). It is not clear, however, how Onsager's argument would be extended to this model and it is likely that it cannot be solved exactly. Widom [37] based on a geometrical theorem by Mermin [38] discussed the decomposition of the multibody potential energy into negative $2m$ -body potentials corresponding to attractive forces and positive $(2m + 1)$ -body

potentials ($m=1, 2, \dots$) corresponding to repulsive forces. Lie [39] proved the asymptotic correctness of the MFA as the dimensionality became infinite for a system of penetrable cubes.

The interactions between unlike particles in the binary mixture are not restricted to be only as hard spheres. The model was later extended to a general interaction, requiring only that this interaction complied with stability requirements [40, 41, 42]. One particularly useful prescription is the gaussian model of Helfand and Stillinger [43] where the Mayer function

$$f_{ab}(r) = \exp(-\beta u_{ab}) - 1 \quad (1-44)$$

for cross a-b interactions, is the gaussian

$$f_{ab}(r) = - \exp(-\alpha^2 r^2) \quad (1-45)$$

The resulting u_{ab} potential is obtained by substitution of (1-44) in (1-45). On transcribing into the one-component version an explicit form of $W(\underline{r}_1, \dots, \underline{r}_N)$ as function of position is obtained [40]

$$W(\underline{r}_1, \dots, \underline{r}_N) = V - \int \left\{ \prod_{i=1}^N (1 - \exp(-\alpha^2 r_i^2)) \right\} d\underline{r} \quad (1-46)$$

which can be expanded as the sum of pair, triplet, etc. interactions as in the original model [35]

$$U(\underline{r}_1, \dots, \underline{r}_N) = \sum_{\text{pairs}} u_2 + \sum_{\text{triplets}} u_3 + \dots \quad (1-47)$$

but with the advantage that the potentials u_n can be written down as explicit functions of position [40]. A second and more useful advantage is that all cluster integrals are readily expressed in closed form [41].

The virial expansion of the one-component model and a mixture of oriented hard cubes was considered by Straley, Cotter, Lie and Widom [44] who obtained the coexistence curve. Melnyk, Rowlinson and Sawford [40] studied the two-component virial expansion in powers of the density and in powers of the activity for the hard-sphere and gaussian models. The critical behaviour of the exact series and the Percus-Yevick (PY) and second-order Percus-Yevick (PY2) approximations [45] was obtained with the use of Padé approximants. The PY approximation yielded a classical critical point in both models. The behaviour of the exact and

PY2 series was irregular for the hard-sphere model but gave a non-classical critical point for the gaussian model. Later Ahn and Lebowitz [46] obtained an exact solution of the PY approximation and confirmed its classical behaviour. The hypernetted-chain (HNC) approximation was studied later [41, 42] and its non-classical nature established.

The volume $W(\underline{r}_1, \dots, \underline{r}_N)$ covered by the spheres placed at random was computed by Monte Carlo simulation by Melnyk and Rowlinson [47, 48] who also studied the cumulant expansion of the potential energy. Other computer experiments were performed on a mixture of molecules of "non-additive diameters", that is, one in which the collision diameters σ_{aa} and σ_{bb} of a-a and b-b interactions are such that the cross diameter σ_{ab} is

$$\sigma_{ab} = \frac{1}{2}(\sigma_{aa} + \sigma_{bb}) + \Delta \quad (1-48)$$

with $\Delta \neq 0$. The penetrable-sphere model corresponds to the limiting case $\sigma_{aa} = \sigma_{bb} = 0$ and $\Delta > 0$. Melnyk and Sawford [48, 49] obtained the equation of state by molecular dynamics simulation [45] and observed a phase separation at high densities.

The mixture model can easily be extended to a ternary system by adding a third component interacting in such a way with the other two that

$$u_{aa} = u_{bb} = u_{cc} = 0$$

and

$$u_{ab} = u_{bc} = u_{cc} = \begin{cases} \infty & \text{for } r < \sigma \\ 0 & \text{for } r > \sigma \end{cases} \quad (1-49)$$

This extension bears no connection with the original penetrable-sphere model other than having the binary mixture as the limit when the density of one of the three components goes to zero. However it will be shown that it can be regarded as a generalization to a continuum system of the three-state Potts model. This ternary mixture model also, in the MFA, resembles closely the symmetric regular solution model of Meijering [50], who studied the phase separation of a ternary mixture which has a Gibbs's free energy of the form

$$G = a(xy + yz + zx) + RT(x \log x + y \log y + z \log z) \quad (1-50)$$

where x , y and z are the mole fractions of the three components and a is an energy parameter. This "model" is purely macroscopic; there is no known microscopic Hamiltonian which leads to (1-50).

Chapter II

THE DISTRIBUTION FUNCTIONS OF THE PENETRABLE-SPHERE MODEL

The penetrable-sphere models of liquid-vapour equilibrium are a class of one-component continuum models in which the particles interact via multibody potentials [34]. The models are isomorphic to two-component mixtures with simple pair potentials. Although the original model was proposed such that the potential between unlike particles in the mixture was that of hard spheres, extensions to more general prescriptions have been developed [40, 41, 42]. Of special interest is the gaussian model where the unlike potential is such that the Mayer function is a gaussian [43].

The isomorphism of the one- and two-component models is demonstrated by showing that their grand partition functions are equal, provided some identifications of their variables are made. These identifications constitute a set of transcription rules by which the properties of one model are mapped into the other. Transcription takes a simple form for approximations such as the mean-field (MFA) or Percus-Yevick (PY) where the direct correlation functions between like particles are zero.

In this chapter we first examine the stability and tempering of the multibody potential and then derive the transcription of the distribution functions and obtain their explicit form in the critical region of the MFA for two prescriptions of the cross potential, the hard-sphere and gaussian models.

II.1 The penetrable-sphere model, stability and tempering of the multibody potential

Consider an ensemble of N identical particles enclosed in a box of volume V and associate with each particle a microscopic sphere of constant volume v_0 centred on it. Those spheres will, in general, interpenetrate.

The total volume covered by such spheres will be a function of the configuration of the particles, denoted $\{N\}$. Let $W\{N\}$ be this function, which is bounded above and below; above when there is no overlapping, and below when all centres coincide,

$$v_0 \leq W\{N\} \leq N v_0 \quad (2-1)$$

The potential energy of the system, $U(N)$, is defined to be proportional to the difference between the volume of N non-overlapping spheres and the function $W(N)$ described above. The function $U(N)$ whose ensemble average is $\bar{U}$ is defined by

$$U(N) = - \frac{\epsilon}{v_0} [Nv_0 - W(N)] \quad (2-2)$$

where $\epsilon > 0$ is a microscopic parameter with units of energy. This is a non-positive function in virtue of (2-1). $U(N)$ is also stable, i.e. there exists a fixed natural number h_A with the property [51]

$$U(N) \geq - N h_A \quad (2-3)$$

for all N and every configuration $\{N\}$. From (2-2) this lower limit is $-\epsilon(N-1)$, thus

$$-\epsilon(N-1) \leq U(N) \leq 0 \quad (2-4)$$

The potential is purely attractive without a hard core. For a pairwise additive function the lower bound would be proportional to the number of pairs, $\frac{1}{2}N(N-1)$, which improperly leads to non-extensive $\bar{U}$. However, the potential of this model is a multibody function, not just a pairwise additive one, which saturates whenever two spheres coincide. It is this property which guarantees that the lower bound of (2-2) is proportional to N , not to N^2 , hence leading to correct Thermodynamics.

In the alternative binary mixture version the intermolecular potentials are defined as

$$\begin{aligned} u_{aa} &= u_{bb} = 0 \\ u_{ab} &= \begin{cases} \infty & r < \sigma_{ab} \\ 0 & r > \sigma_{ab} \end{cases} \end{aligned} \quad (2-5)$$

where σ_{ab} is the collision diameter for particles of unlike species.

The multibody potential $U(N)$ must be short ranged and (at least) weakly tempered, that is, the interaction energy ΔU between two groups

containing N' and N'' molecules must be such that for all N' and N'' and any $\delta > 0$ there exists two fixed positive bounds R_0 and h_B such that

$$\Delta U\{N', N''\} \leq \frac{N' N'' h_B}{r^{3+\delta}} \quad (2-6)$$

whenever $|\underline{r}_i - \underline{r}_j| \geq r \geq R_0$ for all i and j and if $N'N''/r^{3+\delta}$ is sufficiently small [51]. The potential energy (2-2) satisfies both conditions, in fact we take the definition of v_0 and $W\{N\}$ in terms of the pair potential u_{ab} of the mixture version [40]

$$v_0 = - \int f_{ab}(\underline{r}_{oi}) d\underline{r}_o \quad (2-7)$$

$$W\{N\} = v - \int \prod_{i=1}^{N_b} [1 + f_{ab}(\underline{r}_{oi})] d\underline{r}_o \quad (2-8)$$

where f_{ab} is the Mayer function and the particle subscripted zero is of species a and the other $1 \leq i \leq N_b$ particles are of species b, and $N_b = N$. Thus (2-2) may be written as [40, 41]

$$U\{N_b\} = - \frac{\epsilon}{v_0} \int \prod_{i=1}^{N_b} [1 + f_{ab}(\underline{r}_{oi})] d\underline{r}_o \quad (2-9)$$

then

$$\Delta U\{N', N''\} = U\{N', N''\} - U\{N'\} - U\{N''\} \quad (2-10)$$

$$= - \frac{\epsilon}{v_0} \int \left\{ \prod_{i=1}^{N'_b} [1 + f_{ab}(\underline{r}_{oi})] - 1 \right\} \left\{ \prod_{j=1}^{N''_b} [1 + f_{ab}(\underline{r}_{oj})] - 1 \right\} d\underline{r}_o \quad (2-11)$$

and therefore (2-6) is satisfied for the more stringent condition $h_B = 0$. The potential is then said to be strongly tempered. We next obtain the range of $\Delta U\{N', N''\}$. From (2-5) it follows that

$$0 \leq 1 + f_{ab} \leq 1 \quad (2-12)$$

$$1 + \sum_{i=1}^N f_{ab}(r_{oi}) \leq \prod_{i=1}^N [1 + f_{ab}(r_{oi})] \leq 1 + f_{ab}(r_{oi}) \quad (2-13)$$

The first inequality can be proved by induction [35] and the second is trivial. Integration of (2-12) leads, by (2-10), to

$$\int f'_{ab}(r_{oi}) f''_{ab}(r_{oj}) dr_{oi} \leq \frac{v_0}{\epsilon} |\Delta U(N', N'')| \leq \sum_{i=1}^{N'} \sum_{j=1}^{N''} \int f'_{ab}(r_{oi}) f''_{ab}(r_{oj}) dr_{oi} \quad (2-14)$$

and thus ΔU is short-ranged as it is zero for separations of the groups N' and N'' greater than the self-convolution of f_{ab} , which is a measure of the range of the multibody potential.

It should be noticed that the above discussion depends on the property (2-12) of the Mayer function and not on a particular specification of u_{ab} , it therefore may be extended to the general interaction $u_{aa} = u_{bb} = 0$, and $u_{ab} > 0$ such that leads to proper Thermodynamics.

II.2 Transcription of the distribution functions

To demonstrate the equivalence between the two versions of the model and obtain the transcription rules we show that their grand partition functions are equal.

We introduce a convenient set of variables. Let the dimensionless density, pressure-to-temperature ratio, energy density and reciprocal temperature be defined by

$$\rho = v_0 N/V \quad (2-15)$$

$$\pi = p v_0 / kT \quad (2-16)$$

$$\phi = v_0 U / V \quad (2-17)$$

$$\theta = \epsilon / kT \quad (2-18)$$

We define also the dimensionless activity z such that it approaches ρ as ρ tends to zero.

Consider now the two-component grand partition function

$$\Xi_{\text{mix}}(z_a, z_b) = \exp(\pi_{\text{mix}} V/v_o) \quad (2-19)$$

$$= \sum_{N_a=0}^{\infty} \sum_{N_b=0}^{\infty} \frac{1}{N_a! N_b!} \left(\frac{z_a}{v_o} \right)^{N_a} \left(\frac{z_b}{v_o} \right)^{N_b} \iint d\{N_a\} d\{N_b\} \exp(-u_{ab}/kT) \quad (2-20)$$

where $d\{N\}$ represents the element of volume $dr_1 dr_2 \dots dr_N$. When all particles of species b are held fixed the remaining N_a particles constitute an ideal gas moving in a volume $(V - W\{N_b\})$, thus integration over all positions of N_a keeping all particles b fixed yields simply

$$\int d\{N_a\} \exp(-u_{ab}/kT) = [V - W\{N_b\}]^{N_a} \quad (2-21)$$

The sum over N_a gives the exponential factor $\exp(V - W\{N_b\})$. After some rearrangement (2-20) becomes

$$\Xi_{\text{mix}}(z_a, z_b) = e^{\frac{z_a V}{v_o}} \sum_{N_b=0}^{\infty} \frac{1}{N_b!} \left(\frac{z_b}{v_o} \right)^{N_b} \int d\{N_b\} \exp\left(-\frac{z_a W\{N_b\}}{v_o}\right) \quad (2-22)$$

The right hand side of (2-22) is, except for the factor $\exp(z_a V/v_o)$, the definition of the one-component grand partition function if the following identification is made:

$$N_b = N \quad (2-23)$$

$$z_b = ze^{\theta} \quad (2-24)$$

$$z_a = \theta \quad (2-25)$$

thus

$$\Xi_{\text{mix}}(z_a, z_b) e^{-\frac{z_a V}{v_o}} = \Xi(z, \theta) \quad (2-26)$$

Equations (2-23) to (2-26) constitute the transcription rules. We apply them to transcribe the m -body distribution function, which is defined in a one-component fluid by

$$n^{(m)}(1, \dots, m) = \Xi^{-1} \sum_{N \geq m} \frac{1}{(N-m)!} \left(\frac{z}{v_o} \right)^N \int d\{N-m\} \exp\left(\frac{\theta}{v_o}(V-W\{N\})\right) \quad (2-27)$$

Multiplying numerator and denominator by $\exp(\theta V/v_o)$ gives, after some rearrangement

$$n^{(m)}(1, \dots, m) = \exp\left(-\frac{\theta V}{v_o}\right) \sum_{N \geq m}^{-1} \frac{1}{(N-m)!} \left(\frac{ze^{\theta}}{v_o}\right)^N \int d(N-m) \exp\left(\frac{\theta}{v_o} (V - W(N))\right) \quad (2-28)$$

Transcribing into the two-component language with the rules (2.23) to (2.26) and expanding the exponential term gives

$$n^{(m)}(1, \dots, m) = \sum_{\text{mix}}^{-1} \sum_{N_a \geq 0} \sum_{N_b \geq m} \frac{1}{N_a!} \frac{1}{(N_b-m)!} \left(\frac{z_a}{v_o}\right)^{N_a} \left(\frac{z_b}{v_o}\right)^{N_b} \int d(N_a) d(N_b-m) \exp\left(-\frac{u_{ab}}{kT}\right) \quad (2-29)$$

The right hand side of (2-29) is the mixture distribution function $n_{bb\dots b}^{(m)}(1, \dots, m)$. In particular setting $m=1$ yields eq. (2-24) and $m=2$ gives the equality between the pair distribution functions

$$n^{(2)}(1,2) = n_{bb}^{(2)}(1,2) \quad (2-30)$$

A similar procedure can be followed for the mixed distribution function $n_{a\dots ab\dots b}^{(m)}(1, \dots, m)$ but no simple relations as (2-23) or (2-30) are obtained and therefore they are less useful.

The identification of the distribution functions has important consequences in an approximation such as the MFA or PY where $c_{aa} = c_{bb} = 0$. Consider the two-component OZ equations

$$h_{bb}(1,2) = n_a \int h_{ba}(1,3) c_{ab}(3,2) d(3) \quad (2-31)$$

$$h_{ab}(1,2) = c_{ab}(1,2) + n_b \int h_{bb}(1,3) c_{ba}(3,2) d(3) \quad (2-32)$$

where $n_a = N_a/V = \rho_a v_o$ and n_b are number densities. Substitution of (2-31) into (2.32) and vice versa gives

$$h_{ab}(1,2) = c_{ab}(1,2) + n_a n_b \iint h_{ab}(1,4) c_{ab}(3,2) d(4) d(3) \quad (2-33)$$

$$h_{bb}(1,2) = n_a \int c_{ab}(1,3) c_{ab}(3,2) d(3) + n_a n_b \iint h_{bb}(1,4) c_{ab}(4,3) c_{ab}(3,2) d(4) d(3) \quad (2-34)$$

On transcribing h_{bb} to h , ρ_b to ρ and ρ_a to $\theta(1-\rho-\phi)$ we obtain, from (2.34), the one-component OZ equation if we make the identification

$$c(1,2) = \frac{\theta}{v_0} (1-\rho-\phi) \int c_{ab}(1,3) c_{ab}(3,2) d(3) \quad (2-35)$$

The distinctive property of the direct correlation function is its short-rangedness. For pair potentials the range is essentially that of the Mayer function, except from a weak long-ranged tail. In the PY approximation the long-ranged tail is dropped and $c(r)$ is only given by

$$c(r) = f(r) y(r) \quad (2-36)$$

where [17]

$$y(r) = [1 + h(r)] [1 + f(r)]^{-1} \quad (2-37)$$

The PY approximation was originally proposed for systems with pairwise additive potentials. Rushbrooke and Silbert [52] and Rowlinson [53] studied the extension to triplet interactions, but there is no general formulation for a system with multibody potentials. However, the salient feature of the PY approximation is that the range of $c(r)$ is of the order of that of the intermolecular potential [54] and that is exactly what equation (2-35) indicates, as we can see by substitution of (2-36) and comparison with (2-14). Thus transcription preserves the short-rangedness of $c(r)$ and in this sense the one-component $c(r)$ of (2-35) corresponds to a true PY approximation in the system with multibody potentials.

Equation (2-35) takes a simple form in Fourier space. Define the Fourier transform of $c_{ab}(r)$ by

$$v_0 \tilde{c}_{ab}(\underline{k}) = \frac{(\rho_a \rho_b)^{1/2}}{(2\pi)^{3/2}} \int c_{ab}(\underline{r}) e^{i\underline{k} \cdot \underline{r}} d\underline{r} \quad (2-38)$$

and similarly for $\tilde{c}(\underline{k})$. Transforming (2-35) gives

$$(2\pi)^{3/2} \rho \tilde{c}(\underline{k}) = \rho_a \rho_b [(2\pi)^{3/2} \tilde{c}_{ab}(\underline{k})] \quad (2-39)$$

II.3 The mean-field approximation

When all particles assume random positions the behaviour of the system is given by the MFA (section I.1). This approximation is also obtained from the virial expansion of the correlation functions, when all but the second virial coefficient are discarded. In this case [40,44].

$$c_{ab}(r) = f_{ab}(r) \quad (2-40)$$

From (2-35) the one-component function is simply

$$c(r) = \theta(1-\rho-\phi) \ell_2(r) \quad (2-41)$$

where $\ell_2(r)$ is a chain integral

$$\ell_2(r) = v_0^{-1} \int f_{ab}(1,3) f_{ab}(3,2) d(3) \quad (2-42)$$

and from (2-34) the total correlation function is

$$h(r) = \theta(1-\rho-\phi) \ell_2(r) + \rho\theta^2 (1-\rho-\phi)^2 \ell_4(r) + \dots \quad (2-43)$$

$$= \sum_{j=1}^{\infty} \rho^{j-1} \theta^j (1-\rho-\phi)^j \ell_{2j}(r) \quad (2-44)$$

where the $2j$ -chain integral is

$$\ell_{2j}(r) = v_0^{-2j+1} \int \dots \int f_{ab}(1,3) \dots f_{ab}(2j+1,2) d(2) \dots d(2j+1) \quad (2-45)$$

with

$$\ell_2(0) = v_0^{-1} \int r^2 d\underline{r} \quad (2-46)$$

and

$$\int \ell_{2j}(r) d\underline{r} = v_0 \quad (2-47)$$

The correlation functions (2-41) and (2-44) lead to the mean-field equation of state [42]. In fact, the compressibility, given by (1-16), is

$$\left(\frac{\partial \pi}{\partial \rho}\right)_\theta = 1 - n_b \int c(r) d\underline{r} \quad (2-48)$$

where $c(r)$ is in turn given by (2-41). Integration of $\ell_2(r)$ gives simply a factor of v_0 (equation (2-47)), hence

$$\left(\frac{\partial \pi}{\partial \rho}\right)_\theta = 1 - \rho\theta(1-\rho-\phi) \quad (2-49)$$

Combining (2-49) with the identity

$$\left(\frac{\partial \pi}{\partial \rho}\right)_\theta = - \left(\frac{\partial \rho^{-1} \phi}{\partial \rho^{-1}}\right)_\theta \quad (2-50)$$

gives the second order partial differential equation for ϕ

$$\left(\frac{\partial^2 \phi}{\partial \rho^2}\right)_\theta - \left(\frac{\partial \phi}{\partial \log \rho}\right)_\theta + 1-\rho-\phi = 0 \quad (2-51)$$

whose only relevant solution, that is, one for which $\phi \sim \rho^2$ as ρ tends

to zero, gives

$$\phi = 1 - \rho \exp(-\rho) \quad (2-52)$$

which is the result of Widom and Rowlinson (eq.1-43) for the potential energy density of a random configuration, that is, the MFA.

The approximation is exact in infinite dimensions [39,42] and leads to a classical critical point [34] and so the correlation functions are expected to exhibit the classical behaviour.

II.4 The gaussian model

We will consider first the case in which the unlike interactions are gaussian in form (see section I.5). All chain integrals can be integrated in closed form to give, in three dimensions [55]

$$\ell_{2j} = (2j)^{-3/2} \exp\left(-\frac{\alpha^2 r^2}{2j}\right) \quad (2-53)$$

hence

$$c(r) = 2^{-3/2} \theta e^{-\rho} \exp\left(-\frac{1}{2} \alpha^2 r^2\right) \quad (2-54)$$

$$h(r) = 2^{-3/2} \sum_{j=1}^{\infty} j^{-3/2} \rho^{j-1} \theta^j \exp\left(-j\rho - \frac{\alpha^2 r^2}{2j}\right) \quad (2-55)$$

The zeroth moment of $c(r)$ gives the isothermal compressibility and the second moment Debye's persistence length

$$v_0^{-1} \int c(r) d\underline{r} = \theta e^{-\rho} = \rho^{-1} [1 - (\partial \pi / \partial \rho)_\theta] \quad (2-56)$$

$$\alpha^2 R^2 = \frac{1}{6v_0} \int \alpha^2 r^2 c(r) d\underline{r} = \frac{1}{2} \theta e^{-\rho} \quad (2-57)$$

The length R is everywhere comparable with the range of the intermolecular potential as the second moment of $c(r)$ remains finite at the critical point [56].

At large separations the sum in (2-55) is dominated by terms with large j and can be replaced by an integral according to the Euler-MacLaurin theorem [57]

$$\sum_{j=1}^{\infty} f(j) = \int_1^{\infty} f(j) dj + \frac{1}{2} f(1) - \sum_{k=1}^{\infty} \frac{B_{2k}}{(2k)!} f^{(2k-1)}(1) \quad (2-58)$$

where B_{2k} are the Bernoulli numbers. The term $f(1)$ is simply

$$f(1) = \theta(1-\rho-\phi) \quad \ell_2(r) = c(r) \quad (2-59)$$

which is zero at large separations because of the short-rangedness of $c(r)$, therefore

$$h(r) = \frac{1}{2^{3/2}\rho} \int_1^{\infty} (\rho\theta e^{-\rho})^j j^{-3/2} e^{-\frac{a^2 r^2}{2j}} dj \quad (2-60)$$

With the change of variable $t = j^{-2}$ and the definitions

$$a^2 = \frac{1}{2} \alpha^2 r^2 \quad (2-61)$$

$$b^2 = \rho - \log(\rho\theta) \quad (2-62)$$

equation (2-60) becomes

$$h(r) = \frac{1}{2^{3/2}\rho} \int_0^1 \exp(-a^2 t^2 - \frac{b^2}{t^2}) dt \quad (2-63)$$

The integration can be performed for real values of a and b (b is real throughout the whole of the one-phase region) to give [58]

$$h(r) = \left(\frac{\sqrt{\pi}}{2}\right) \frac{1}{4\rho a} \{e^{2ab} [\operatorname{erf}(a+b) - 1] + e^{2ab} [\operatorname{erf}(a-b) + 1]\} \quad (2-64)$$

where $\operatorname{erf}(x)$ is the error function.

For large values of r the error functions assume the asymptotic form [58]

$$\operatorname{erf}(a+b) - 1 \rightarrow -\frac{\exp(-(a+b)^2)}{\sqrt{\pi}(a+b)} \quad (2-65)$$

and

$$\operatorname{erf}(a-b) + 1 \rightarrow 2 - \frac{\exp(-(a-b)^2)}{\sqrt{\pi}(a+b)} \quad (2-66)$$

hence (2-64) is, for large r

$$h(r) = \frac{1}{\sqrt{2}} \frac{1}{2\rho a} \left[e^{-2ab} - \frac{b e^{-(a^2+b^2)}}{a^2 - b^2} \right] \quad (2-67)$$

$$\approx \frac{1}{2\sqrt{2}\rho} \frac{e^{-2ab}}{a} \quad (2-68)$$

as the second exponential dies out more quickly than the first.

Transforming back to the usual variables we get

$$h(r) = \frac{1}{2\rho\alpha} \frac{e^{-\kappa r}}{r} \quad (2-69)$$

$$= \left(\frac{\theta}{\rho e^{\rho}} \right) \frac{v_0}{4\pi R^2} \frac{e^{-\kappa r}}{r} \quad (2-70)$$

κ is an inverse correlation length (discussed in section I.2, the equation (1-19) there) defined by comparison between (2-68) and (2-69) as

$$\frac{1}{2} \alpha^{-2} \kappa^2 = \rho^{-1} \log(\rho\theta) \quad (2-71)$$

The correlation length $\xi = \kappa^{-1}$ is a measure of the average distance in a fluctuation. In the above discussion it has only been regarded as a parameter entering in the exponential damping of $h(r)$, but it is a physical quantity of central importance in the scaling hypothesis [21,22]. According to that hypothesis it is the longest and only relevant length in critical phenomena, which accounts for the temperature dependence near T_c of all quantities, that is, the temperature dependence of any physical quantity in the critical region can be deduced by studying the way it behaves under a change of scale [59]. We will not enter in a detailed discussion of the scaling hypothesis, which the MFA surely satisfies, but will only show how another important length, the mean range of order, becomes asymptotically equal to ξ .

The mean range of order, λ , is defined by [29,56]

$$\alpha^2 \lambda^2 = \frac{\rho}{6v_0} \frac{\int \alpha^2 r^2 h(r) dr}{1 + \frac{\rho}{v_0} \int h(r) dr} \quad (2-72)$$

Integration of the OZ equation, (1-6), gives

$$\int r^2 h(r) d\underline{r} = \left[1 + \frac{\rho}{v_0} \int h(r) d\underline{r} \right]^2 \int r^2 c(r) d\underline{r} \quad (2-73)$$

$$= \frac{\left(1 + \frac{\rho}{v_0} \int h(r) d\underline{r} \right) \int r^2 c(r) d\underline{r}}{1 - \frac{\rho}{v_0} \int c(r) d\underline{r}} \quad (2-74)$$

where the last step results from Fourier inversion of (1-15).
Therefore

$$\alpha^2 \lambda^2 = \frac{\rho}{6v_0} \frac{\int \alpha^2 r^2 c(r) d\underline{r}}{1 - \frac{\rho}{v_0} \int c(r) d\underline{r}} \quad (2-75)$$

$$= \rho \alpha^2 R \left(\frac{\partial \pi}{\partial \rho} \right)_\theta^{-1} \quad (2-76)$$

$$= \frac{\frac{1}{2} \rho \theta e^{-\rho}}{1 - \rho \theta e^{-\rho}} \quad (2-77)$$

From (2-71)

$$\exp \left(\frac{1}{2} \alpha^{-2} \kappa^2 \right) = \rho \theta e^{-\rho} \quad (2-78)$$

thus

$$\alpha^2 \lambda^2 = \frac{\frac{1}{2} \exp \left(-\frac{1}{2} \alpha^{-2} \kappa^2 \right)}{1 - \exp \left(-\frac{1}{2} \alpha^{-2} \kappa^2 \right)} \quad (2-79)$$

$$= \frac{1}{2} \left(\exp \frac{\kappa^2}{2\alpha^2} - 1 \right)^{-1} \quad (2-80)$$

Near the critical point, where κ is small,

$$\lambda\kappa = 1 \quad (2-81)$$

There is, therefore, only one correlation length, since λ and κ^{-1} become asymptotically equal as the critical point is approached. Scaling relations among the critical indices are satisfied with the exponents taking their classical values $\alpha = 0$, $\beta = \frac{1}{2}$, $\gamma = 1$.

II.5 The hard-sphere model

The hard-sphere model in which unlike interactions are hard spheres conforms to the same pattern. The chain integral (2-42) is now the common volume covered by two spheres, each of volume v_0 , separated by a distance r . $c(r)$ is given by

$$c(r) = \begin{cases} \theta(1-\rho-\phi) \left[1 - \frac{3}{2} \left(\frac{r}{2\sigma} \right) + \frac{1}{2} \left(\frac{r}{2\sigma} \right)^3 \right] & r \leq 2\sigma \\ 0 & r > 2\sigma \end{cases} \quad (2-82)$$

The total correlation function is found first by taking the Fourier transform of $c(r)$

$$\tilde{c}(k) = \frac{4\pi}{k} \frac{\theta e^{-\rho}}{v_0} \int_0^\infty r \left[1 - \frac{3}{2} \left(\frac{r}{2\sigma} \right) + \frac{1}{2} \left(\frac{r}{2\sigma} \right)^3 \right] \sin(kr) dr \quad (2-83)$$

$$= \frac{\theta e^{-\rho}}{(2\pi)^{3/2}} \left[\frac{3 j_1(k\sigma)}{k\sigma} \right] \quad (2-84)$$

where $j_1(k\sigma)$ is the spherical Bessel function of the first kind and order one. We then solve the OZ equation in Fourier space for $\tilde{h}(k)$

$$\tilde{h}(k) = \frac{\tilde{c}(k)}{1 - \rho \tilde{c}(k)} \quad (2-85)$$

$$= \frac{\theta e^{-\rho} (k\sigma)^{-2} (3 j_1(k\sigma))^2}{1 - \rho \theta e^{-\rho} (3 j_1(k\sigma)/k\sigma)^2} \quad (2-86)$$

Transforming back to configuration space gives

$$h(r) = \frac{2\theta e^{-\rho}}{3\pi} \int_0^{\infty} \frac{j_0(kr) \left[3 j_1(k\sigma) \right]^2 d(k\sigma)}{1 - \rho \theta e^{-\rho} \left[\frac{3 j_1(k\sigma)^2}{k\sigma} \right]} \quad (2-87)$$

The function $h(r)$ is not analytical (as $h(r) \rightarrow c(r)$ as $\rho \rightarrow 0$ and $c(r)$ is discontinuous at $r = 2\sigma$), but it can be easily integrated numerically by Simpson's rule. Its numerical solution is shown in fig.5.

Nonetheless, for large separations, corresponding to small k , the integral can be worked out by using the asymptotic expression [60]

$$j_1(x) \approx \frac{1}{3} x \exp(-x^2/10) \quad (2-88)$$

hence

$$h(r) = \frac{2\theta e^{-\rho} \sigma^3}{3\pi} \int_0^{\infty} \frac{j_0(kr) [k^2 \exp(-\frac{1}{5} k^2 \sigma^2)]}{1 - \rho \theta e^{-\rho} \exp(-\frac{1}{5} k^2 \sigma^2)} dk \quad (2-89)$$

Expanding the denominators gives

$$h(r) = \frac{2\theta e^{-\rho} \sigma^3}{3\pi} \int_0^{\infty} j_0(kr) k^2 \exp(-\frac{1}{5} k^2 \sigma^2) \sum_{n=0}^{\infty} (\rho \theta e^{-\rho})^n \exp(-\frac{n k^2 \sigma^2}{5}) dk \quad (2-90)$$

The spherical Bessel function $j_n(z)$ is related to the Bessel function of the first kind and fractional order by [61]

$$j_n(z) = \sqrt{\frac{2\pi}{z}} J_{n+\frac{1}{2}}(z) \quad (2-91)$$

Making use of (2-91) with $n = 0$ we write, after collecting terms

$$h(r) = \frac{2\theta e^{-\rho} \sigma^3}{3\pi} \sum_{m=1}^{\infty} (\rho \theta e^{-\rho})^{m-1} \frac{(\frac{1}{2}\pi)^{\frac{1}{2}}}{r^{\frac{1}{2}}} \int_0^{\infty} J_{\frac{1}{2}}(kr) k^{\frac{3}{2}} \exp\left(-\frac{mk^2 \sigma^2}{5}\right) dk \quad (2-92)$$

The value of the integral is [62]

$$\int_0^{\infty} J_{\frac{1}{2}}(kr) k^{\frac{3}{2}} \exp\left(-\frac{mk^2 \sigma^2}{5}\right) dk = \frac{r^{\frac{1}{2}}}{\left(\frac{2m\sigma^2}{5}\right)^{\frac{3}{2}}} \exp\left(-\frac{r^2}{4m\sigma^2/5}\right) \quad (2-93)$$

therefore (2-92) is transformed into the sum

$$h(r) = \frac{5^{3/2}}{6\pi^{1/2}\rho} \sum_{m=1}^{\infty} \rho^m \theta^m m^{-3/2} \exp\left(-\rho m - \frac{5r^2}{4\sigma^2 m}\right) \quad (2-94)$$

which is identical to the sum in the gaussian model, eq. (2-55), and the same procedure is followed for its asymptotic evaluation. The range of the potential is in this case $(2/3)^{\frac{1}{2}}\sigma$ instead of σ^{-1} .

For large m the sum is replaced by the integral

$$h(r) = \frac{5^{3/2}}{3\pi^{1/2}\rho} \int_0^1 \exp\left(-a^2 t^2 - \frac{b^2}{t^2}\right) dt \quad (2-95)$$

with

$$a^2 = \frac{5r^2}{4\sigma^2} \quad (2-96)$$

$$b^2 = \rho - \log(\rho\theta) \quad (2-97)$$

whose asymptotic behaviour leads to

$$h(r) = \frac{5\sigma}{3\rho} \frac{e^{-\kappa r}}{r} \quad (2-98)$$

which is identical to (2-69) with the appropriate range of the potential. The inverse correlation length is given by

$$\frac{1}{5} \sigma^2 \kappa^2 = \rho - \log(\rho\theta) \quad (2-99)$$

and λ by

$$\sigma^{-2} \lambda^2 = \frac{\frac{1}{5} \rho \theta e^{-\rho}}{1 - \rho \theta e^{-\rho}} \quad (2-100)$$

Thus we have again

$$\sigma^{-2} \lambda^2 = \frac{1}{5} (\exp(\frac{1}{5} \sigma^2 \kappa^2) - 1)^{-1} \quad (2-101)$$

which reduces to $\lambda\kappa = 1$ for small κ .

II.6 Discussion

Equations (2-80) for the gaussian model and (2-101) for the hard-sphere model relate the correlation lengths λ and κ^{-1} and exhibit their asymptotic identity as the critical point is approached. The form of those equations depend only on the range of the potential and may have wider validity than this class of models.

Figures 6 to 8 illustrate the correlation functions and their Fourier transforms in the one- and two-component versions of the hard-sphere model.

$h(r)$ rapidly approaches the limiting value of $(5\sigma/3r)$ when, at $\rho = \rho_c$ and $\theta = \theta_c$, r increases. This is the limit contained in equation (2-70).

The critical point is, by the nature of the MFA, classical. We will obtain and discuss the critical behaviour of two more complete approximations, the PY and HNC, in chapter V. They are found to predict critical points of very different nature, the PY being classical as the MFA while the HNC being non-classical, in closer agreement with experimental systems. This distinction is maintained in a more realistic system where the molecules interact with (12,6) Lennard-Jones potentials.

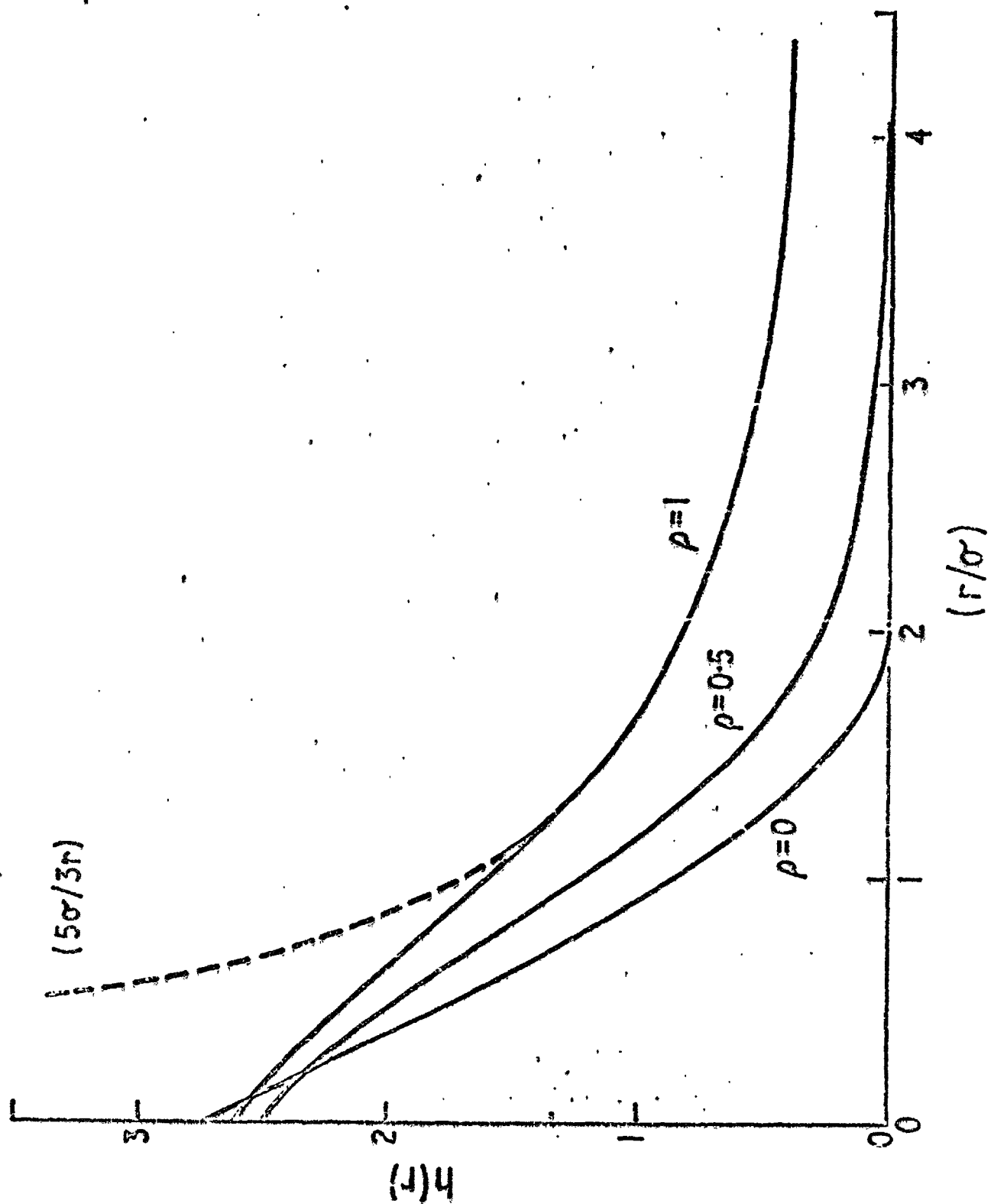


Figure 5 Total correlation function of the penetrable-sphere model in the mean-field approximation. The dotted line is the asymptotic limit at the critical point.

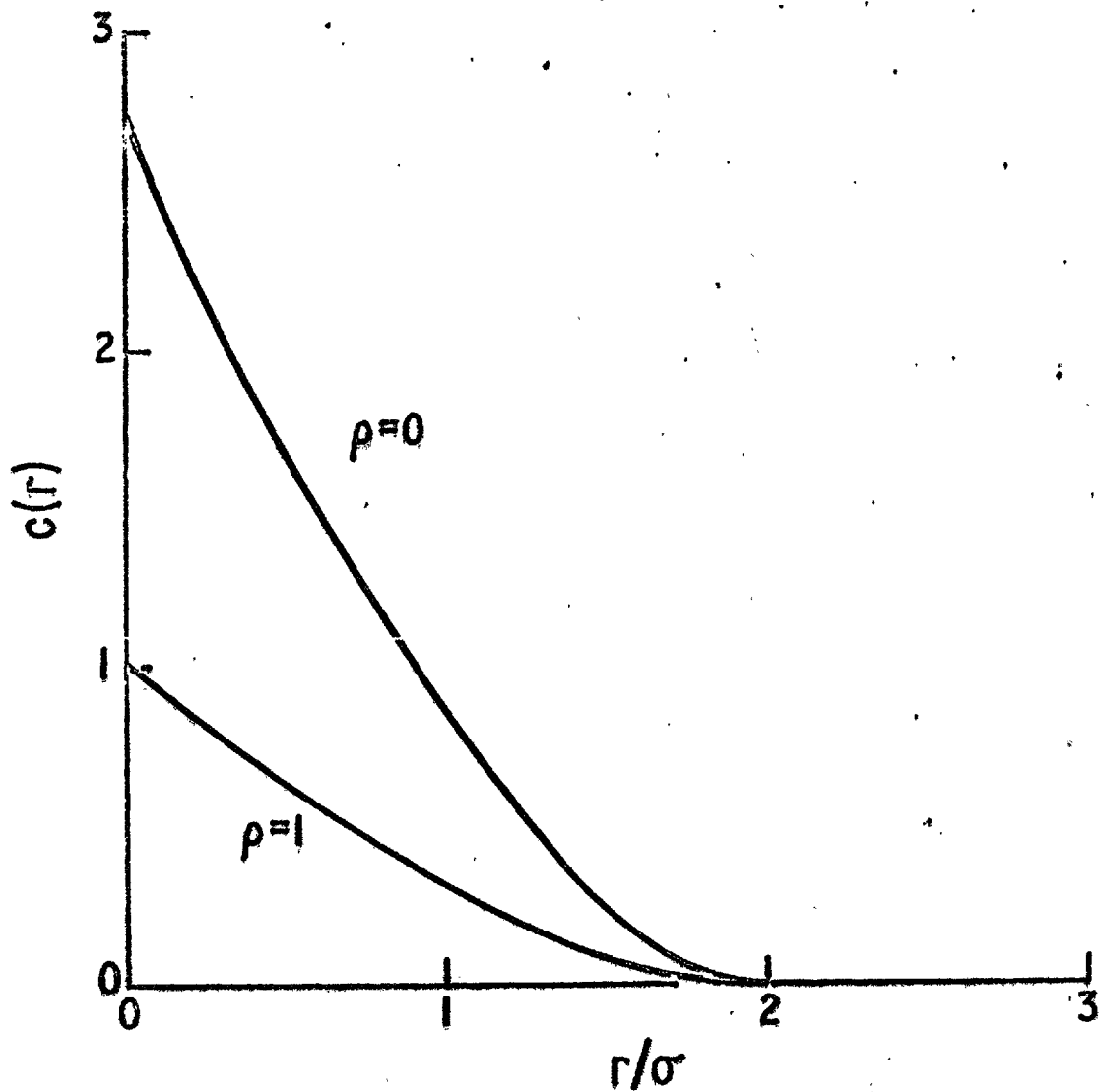


Figure 6 . One-component direct correlation function of the penetrable-sphere model in the MFA in the limits of zero and critical density.

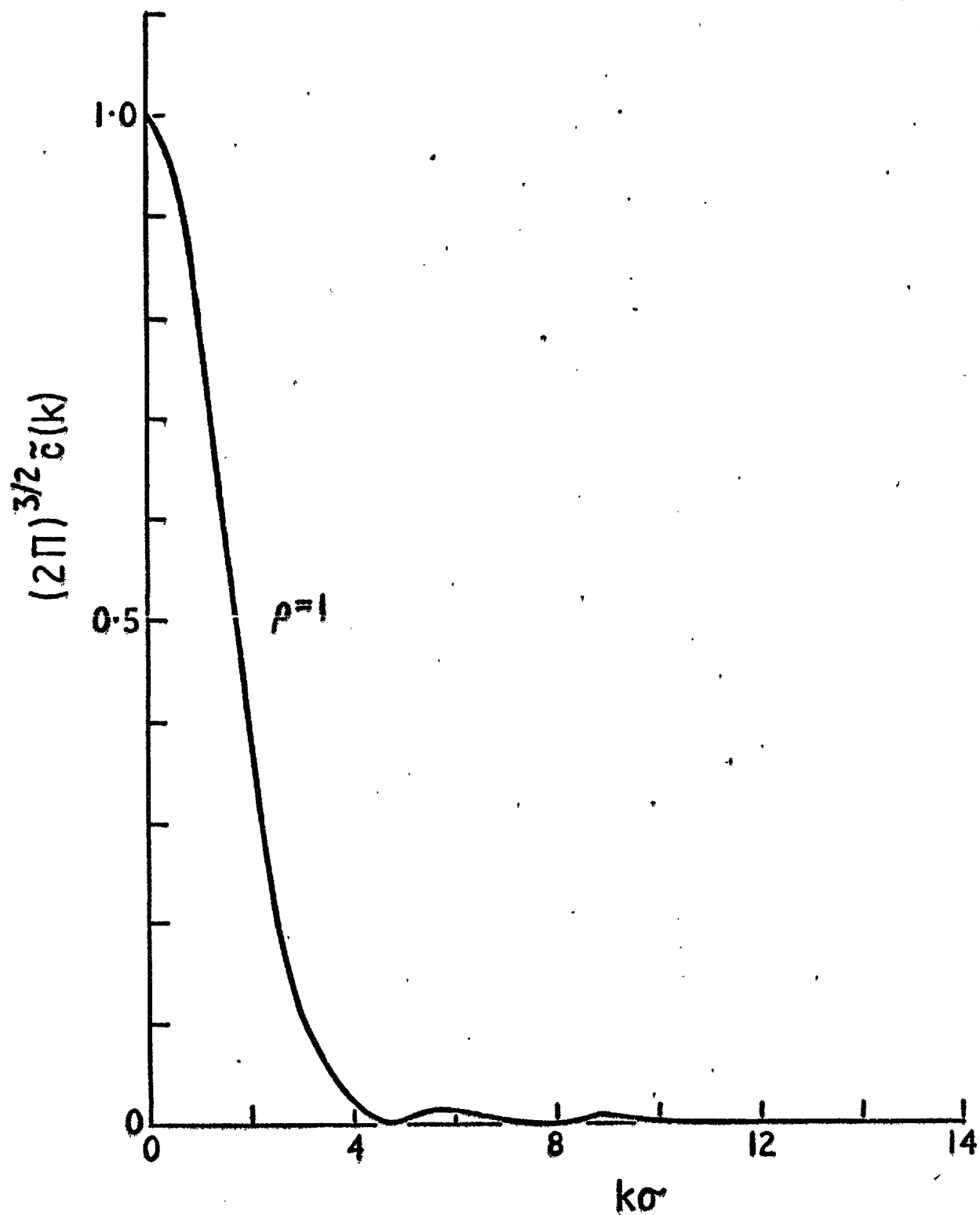


Figure 7 Fourier transform of the one-component direct correlation function in the MFA.

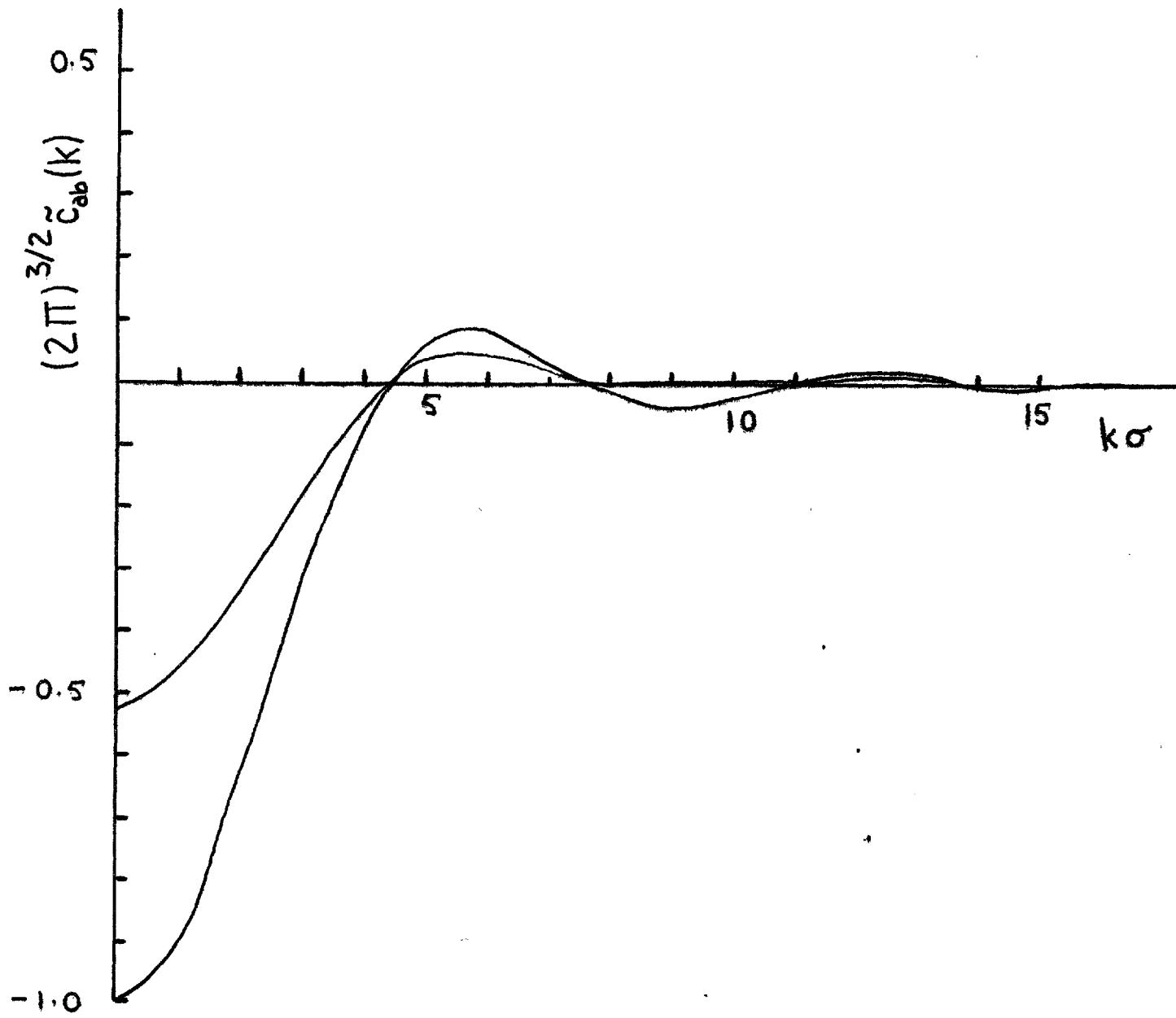


Figure 8 Fourier transform of the two-component direct correlation function.

Chapter III

A TERNARY MIXTURE CONTINUUM MODEL

The mathematical simplicity of the two-component version of the penetrable-sphere model suggests that with the inclusion of a third component a simple and physically adequate model to study phase equilibria in ternary fluid mixtures would be obtained. The extended model may be regarded as a generalization to continuum systems of the three-states Potts model [31] outlined in chapter I, in the same sense that the original penetrable-sphere model is a generalization of the lattice gas [34].

The model is defined by the intermolecular potentials. As in the binary mixture, only unlike molecules interact and do so via simple pair potentials. It was shown in Chapter II that any purely repulsive potential leading to proper thermodynamics may be acceptable; in practice the two most useful are that of the hard sphere model and that of the gaussian model, both leading to temperature-independent configuration energy.

We set then

$$u_{aa} = u_{bb} = u_{cc} = 0 \quad (3-1)$$

$$\text{and } u_{ab} = u_{bc} = u_{ca} > 0 \quad (3-2)$$

with $u_{\alpha\beta}$ ($\alpha \neq \beta$) either

$$u_{\alpha\beta} = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \quad (3-3)$$

or

$$u_{\alpha\beta} = -kT \log (1 - e^{-\gamma^2 r^2}) \quad (3-4)$$

The model has a three-fold symmetry in the three components, which play identical roles. The symmetry reduces considerably the complexity of the calculations and is closely analogous to that of the Potts model and Meijering's regular solutions with equal and positive energy parameters.

The mixture undergoes two phase transitions of interest; one is of higher order (continuous) where three phases vanish in a tricritical point above which there are three-phase equilibria. The other is of first order (discontinuous) and occurs at still higher pressure (see ref. 12 for the classification of phase transition). On lowering the pressure from above the second transition a three-phase region splits into a complex configuration of one-, two- and three-phase regions, the transition point being an equilibrium quadruple point, i.e. one where four phases coexist.

Phase diagrams in ternary systems are difficult to visualize since four variables are necessary to define a state, although in this model with temperature-independent configuration energy only three variables are independent, as the temperature is irrelevant. The pressure-to-temperature ratio will then be treated as a single variable. A useful coordinate system on which to draw phase diagrams is the Möbius triangular system where the compositions of the three components are plotted in an equilateral triangle, the vertices of which represent pure components and the sides binary mixtures; one point inside the triangle represent a state with composition of each component proportional to the perpendicular distances to the sides.

The phase diagram of this continuum mixture is shown in Figure 9. In Fig. 9a the pressure is such that the whole of the interior of the triangle represents a single homogeneous phase. The binary critical points are in the middle of each side marked by dots. When the pressure is raised two-phase crescents develop from the sides (Fig. 9b) which expand until the pressure of the first transition of interest, that of higher order, is reached. Above this pressure three-phase equilibria form, therefore the transition corresponds to a tricritical point. Above the tricritical pressure the phase diagram is complex, showing regions of one-, two-, and three-phase equilibria (Fig. 9c). As the pressure is further raised the two- and three-phase regions expand until the two-phase regions developing from the sides of the three-phase triangle touch at the lines of symmetry (Fig. 9d) and at higher pressures join forming strips (Fig. 9e). At still higher pressures the three-phase regions reach the lines of symmetry (Fig. 9f). It is at this

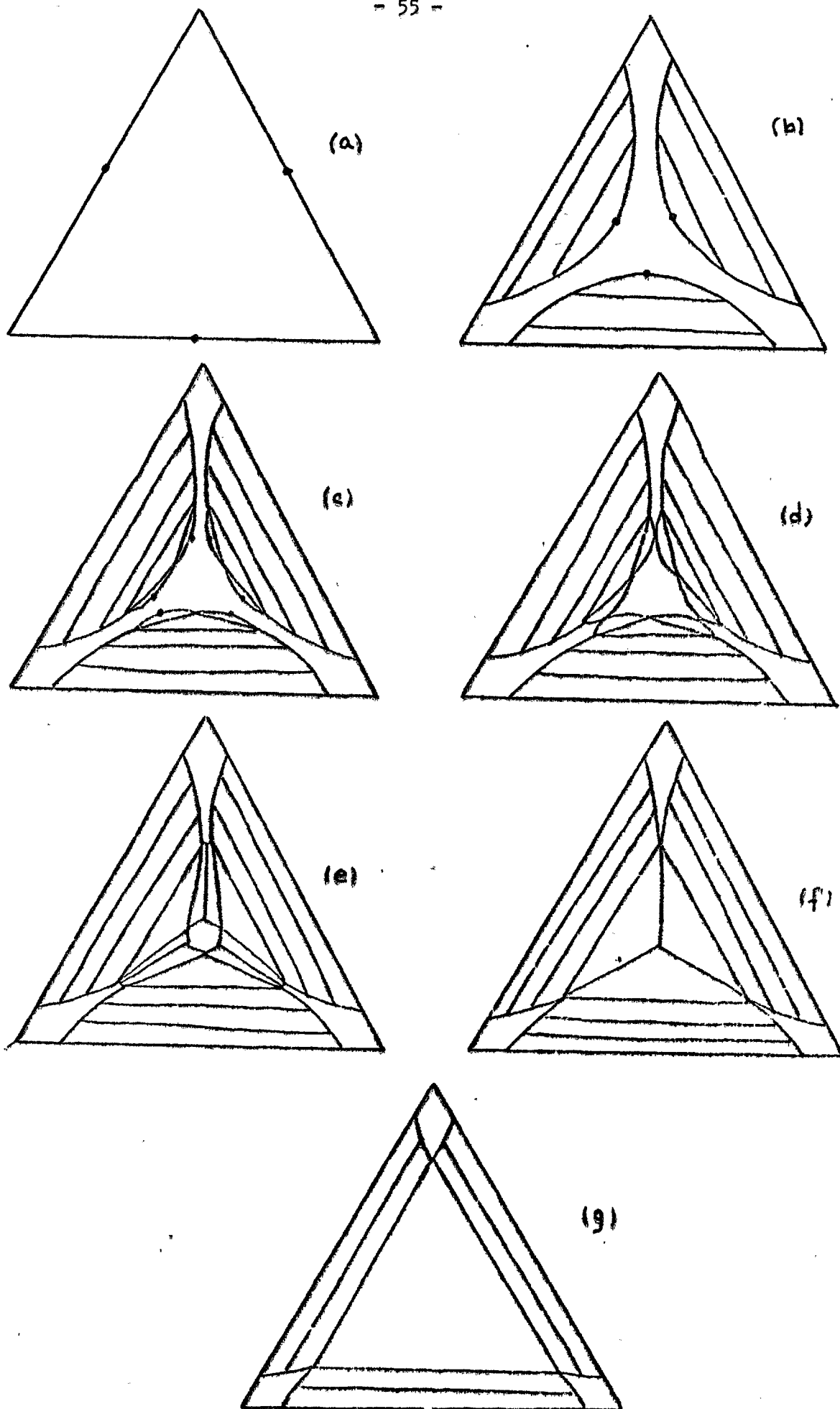


Figure 9 Phase diagram of a ternary mixture with "normal" tricritical point.

pressure when the second transition of interest occurs; it is a first-order (discontinuous) transition where no critical fluctuations occur; four-phase equilibria between an equimolar and a-rich, b-rich and c-rich phases is established; for any higher pressure a single three-phase region forms in the middle, which expands filling the whole of the triangle at infinite pressure (or zero temperature).

Such geometry has been discussed earlier [63]. Tricritical points were discussed theoretically in 1926 [64] but were discovered experimentally much later [65] and the behaviour of thermodynamic variables as the tricritical point is approached has been considered only in the last few years. Meijering [50] obtained a phase diagram identical with the one shown in Fig.9 for a hypothetical thermodynamic system of regular solutions. Widom and Griffiths [65] pointed out the similarities between tricritical points in fluid mixtures, magnetic systems and the mixture $\text{He}^3 - \text{He}^4$ and suggested an examination of tricritical exponents and dynamical properties to see in which way they differ from ordinary critical points (i.e. those where two phases vanish simultaneously). Riedel and Wegner [66,67] had found from renormalization group analysis [59] that tricritical exponents should not differ from their classical (i.e. mean-field) values by more than logarithmic corrections, in contrast with ordinary critical point exponents [12]. An equivalent conclusion was drawn by Griffiths [33] who discussed the experimental data cited in Ref. [65]. He put forward a phenomenological model of the type proposed by Landau [8]. The free energy Ψ is expanded in powers of a one-dimensional order parameter ψ by

$$\Psi = a_1\psi + a_2\psi^2 + a_3\psi^3 + a_4\psi^4 + \psi^6 \quad (3-5)$$

where the a_j are such that they take identical values in coexisting phases while ψ does not. According to the convention of Griffiths and Wheeler [68] the former belong to the class of "field" variables while the second belong to the "density" variables; examples of the first are the pressure, temperature and chemical potentials, of the second are the number densities, volume and entropy density. The parameters a_j are then assumed to be linear combinations of some fields which vanish at the tricritical point. As it is evident from (3-5) the free energy Ψ is a generalised homogeneous function of the a_j and therefore has a scaling property, with a set of exponents derived from it.

One important consequence of Griffiths's model concerns the shape of the three-phase region in the tricritical neighbourhood. Analysis of the relative magnitude of the a_j (or equivalently, the linear combinations of the field associated with them) show that the three-phase triangle shrinks in such a way that one edge vanishes more rapidly than the dimension perpendicular to it, and this longest edge is nearly parallel to a unique direction in density space (Figure 10) [33,69]. The difference of densities of the vertices of the longest edge vanish as $(T - T_{TC})^{\frac{1}{2}}$ (T_{TC} is the tricritical temperature and $\beta_1 = \frac{1}{2}$ is the tricritical exponent) and the direction perpendicular vanishes as $(T - T_{TC})$ (exponent $\beta_2 = 1$). Recent measurements of the system benzene-ethanol-water-ammonium sulfate [70] support the view of a unique direction in composition space singled out by the vanishing of the three-phase triangles; the measured tricritical exponents were $\beta_1 = 0.4$ and $\beta_2 = 1.0$.

A rather different picture was obtained by Straley and Fisher [32] in their series analysis of the two-dimensional (square lattice) three-states Potts model. Both the nature of the tricritical point and the underlying geometry of the phase diagram disagree with Griffiths's view. According to their results the system undergoes only one phase transition, which is continuous and occurs in place of the quadruple point of Fig. 9f. The phase diagram is shown in Figure 11. At low pressures, Fig. 11a, the phase diagram is identical to that of Fig. 9b. On raising the pressure, though, the two-phase crescents, instead of developing the complex geometry of the previous case, grow, deforming continuously (Fig. 11b), until all three touch at the centre in a single tricritical point (Figure 11 d). This three-fold symmetric point is incompatible with a unique direction in density (or composition) space. For higher pressures the tricritical point splits into a three-phase triangle as in Fig. 9g, but without passing through the quadruple point of Figure 9f.

The phase diagrams of Figures 9 and 11 are clearly different. For the purposes of classification we call the class of models following the former the "normal" tricritical-point models while those following the later are the "anomalous" tricritical-point models. (Straley and Fisher [32] proposed the name of "anomalous" tricritical point for the one discovered by them).

Evidence supporting both views has been produced by model studies [32, 33, 65-78] and recently by experimental determination of the tricritical exponents [70]. Some of these works have been devoted to

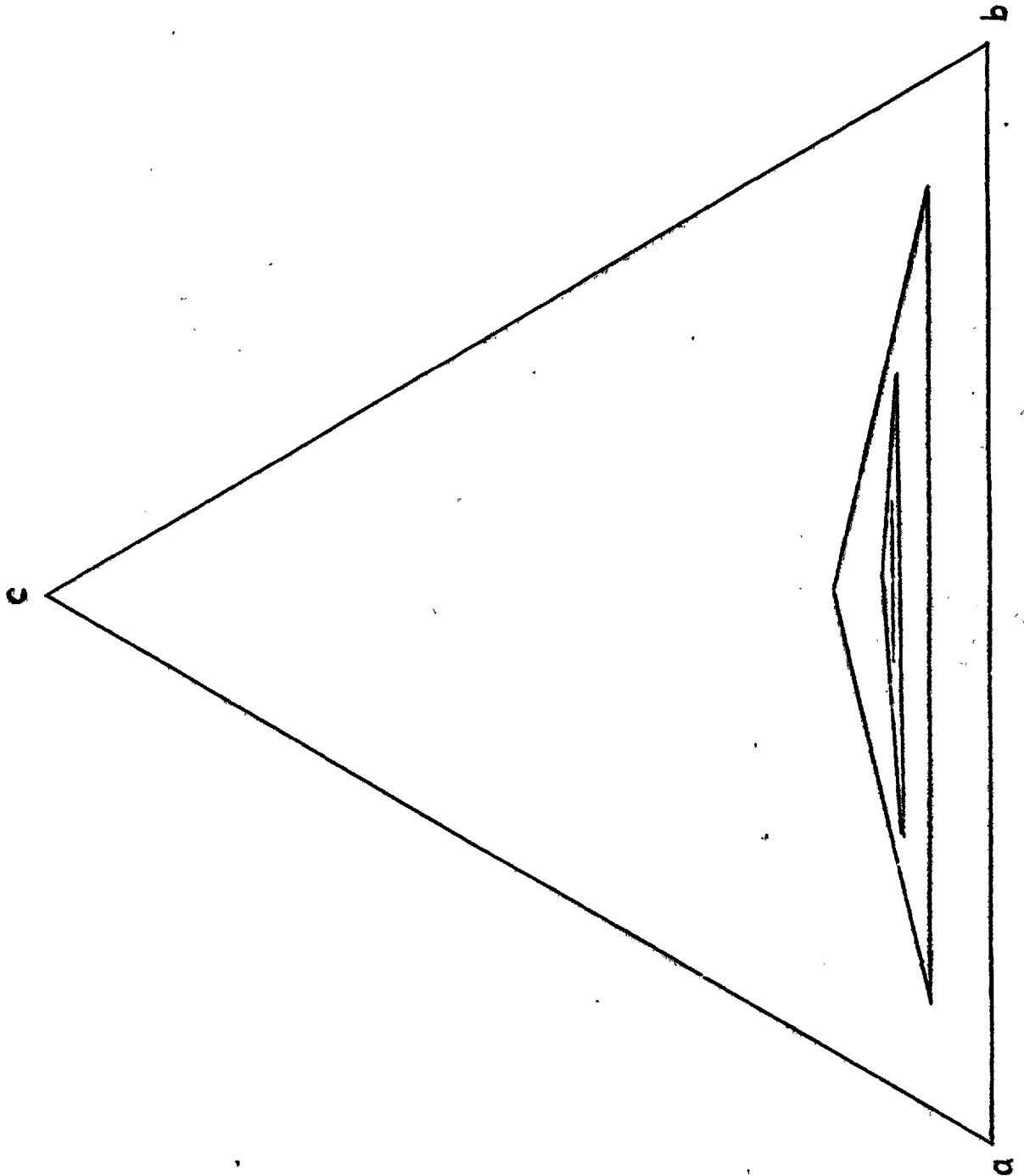


Figure 10 Shrinking of the three-phase region in the neighbourhood of a normal tricritical point. A well-defined direction is singled out.

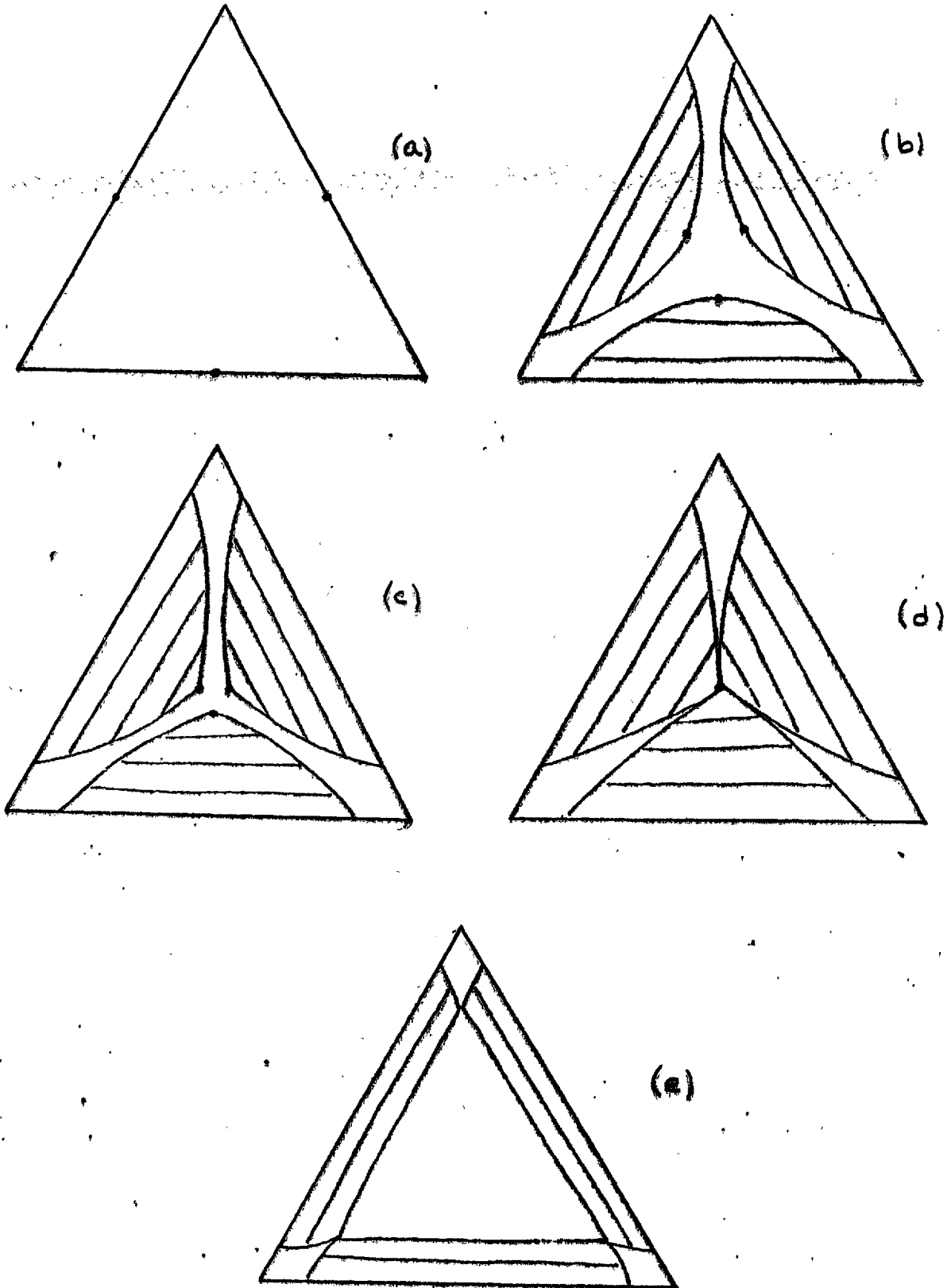


Figure 11 Phase diagram of a ternary mixture with "anomalous" tricritical point.

determine the order of the transition when, on lowering the pressure, the single three-phase region in the middle (Figs. 9g or 11e) splits. In the class of "normal" models this transition is of first order (discontinuous) since it occurs at a point of four-phase equilibrium where no critical fluctuations are involved; on lowering the pressure from that point the complex phase diagram of Fig. 9e is obtained and for a somewhat lower pressure three asymmetrical tricritical points are formed.

For the "anomalous" class of models the only transition is of higher order (continuous) where three phases vanish on an equal footing in a three-fold symmetrical tricritical point.

Consequently the question of whether there is a quadruple point and three asymmetrical tricritical points or only one symmetrical tricritical point is equivalent to asking whether the first transition appearing when lowering the pressure from the central three-phase region is of first or higher order.

Golner [71] studied a continuous generalization of the two-, three- and four-dimensional Potts model replacing the q discrete states by a three-fold symmetric probability distribution. Using the $\eta = 0$ approximation to the renormalization group recursion formula (where η is the Fisher critical exponent related to the decay of $h(r)$) he found a first-order transition corresponding to the "normal" picture of Figure 9. He concluded that the order of the transition should be a general feature of systems with three-fold symmetry, at least in the approximation $\eta = 0$. Ditzian and Oitmaa [72] discussed the high-temperature series expansion of the spin-1 Ising model with biquadratic interactions such that include the Potts model. The order of the transition depends on the magnitude of the biquadratic interactions parameter, which gives rise to "regions" of first and higher order transitions; the three-states Potts model lies in the border of the first order transition for $d = 3$. Sivardière and Lajzerowicz [73] found that the spin-1 lattice gas model for symmetric binary parameters predicts normal phase diagrams, that is first order transition.

The "anomalous" phase diagram or, equivalently, the picture of the higher order transition is also well supported. Baxter [74] obtained exact expressions for the free energy and critical temperature of a two-dimensional q -state Potts model and demonstrated rigorously that for $q > 4$ the model has a first order transition but for $q \leq 4$ the transition is of higher order. Enting [75] performed high-field series expansions of the three-states Potts model for square, simple cubic,

body-centred cubic, triangular and face-centred cubic lattices; the latter was used to study the transition. Although the results are scattered and give a critical point above the one predicted by high-temperature expansions, he interpreted the transition as a higher-order one. Straley [76] investigated the three-dimensional Potts model on a simple cubic lattice with low- and high-temperature expansions; both have divergences on the same temperature range and the free energy and the internal energy bridge continuously from the low- to the high-temperature series, which is evidence of a higher-order transition; however anomalies in the high-temperature series cast some doubt on their validity. Kim and Joseph studied the q -state Potts model in two and three dimensions [77] and the spin-1 Schrödinger exchange model [78] which is a generalization of the spin- $\frac{1}{2}$ Heisenberg model [79] in the same way that the Potts model is a generalization of the spin- $\frac{1}{2}$ Ising model. The problem in the Potts model was approached by investigating the derivatives of the free energy with respect to an order parameter and the temperature; the authors claim to have good evidence of a higher order transition in the high-temperature series for $q \geq 3$. With regard to the Schrödinger model they found mean-field-like behaviour for the high-temperature series of the free energy on a face-centred cubic lattice.

The order of the transition is, thus, still subject to controversy; there seems to be no decisive argument for either. In the next two chapters the phase behaviour of the ternary model described at the beginning of this chapter is studied in detail. The model exhibits a "normal" phase diagram in the MFA and that picture is not altered when up to six virial coefficients are considered.

III. 1 The Mean-Field Approximation, basic equations

The mean field approximation corresponds to restricting the virial series to the first term after the perfect gas contribution (Chapter II). The Helmholtz free energy, A , is then given by

$$A(T, V, N) = A_0(T, V, N) + \frac{kT}{V} \sum_{\alpha=a, b, c} \sum_{\beta=a, b, c} N_{\alpha} N_{\beta} B_{\alpha\beta} \quad (3-6)$$

where N is the composition vector (N_a, N_b, N_c) , A_0 is the free energy of a mixture of perfect gases at the same temperature and $B_{\alpha\beta}$ is the molecular second virial coefficient which is in this model [40]

$$B_{\alpha\beta} = \frac{1}{2} v_0 (1 - \delta_{\alpha\beta}) \quad (3-7)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta and v_0 is a constant microscopic volume defined by the intermolecular potential $u_{\alpha\beta}$.

The free energy of a mixture of perfect gases is given by [80]

$$A_0(T, V, N) = \sum_{\alpha=a,b,c} N_{\alpha} \mu_{\alpha}^{\ominus} - kT \sum_{\alpha=a,b,c} \log Z_{\alpha}(T, V, N) \quad (3-8)$$

where $\mu_{\alpha}^{\ominus}$ is the chemical potential of particles of species α in a reference state denoted $(\ominus)$ and $Z_{\alpha}(T, V, N)$ is the canonical partition function given by

$$Z_{\alpha}(T, V, N) = \frac{V^{\frac{N_{\alpha}}{\alpha!}}}{N_{\alpha}!} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3N_{\alpha}}{2}} \quad (3-9)$$

Substitution of (3-9) in (3-8) gives

$$A_0(T, V, N) = \sum_{\alpha} N_{\alpha} \mu_{\alpha}^{\ominus} + kT \sum_{\alpha} N_{\alpha} \left\{ \log \left[\frac{N_{\alpha} kT}{p^{\ominus} V} \right] - 1 \right\} \quad (3-10)$$

where the reference pressure has been chosen to be

$$\frac{p^{\ominus}}{kT} = \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \quad (3-11)$$

So the free energy of the system is, in full

$$\frac{A(T, V, N)}{kT} = \sum_{\alpha} N_{\alpha} \left[\frac{\mu_{\alpha}^{\ominus}}{kT} + \log \left[\frac{N_{\alpha} kT}{p^{\ominus} V} \right] - 1 \right] + \frac{v_0}{V} (N_a N_b + N_b N_c + N_c N_a) \quad (3-12)$$

All the thermodynamic information is contained in this equation; the pressure and chemical potential follow by differentiation

$$p = - \left(\frac{\partial (A/kT)}{\partial V} \right)_{T, N} \quad (3-13)$$

$$= \frac{N_a + N_b + N_c}{V} + \frac{v_o (N_a N_b + N_b N_c + N_c N_a)}{V^2} \quad (3-14)$$

and

$$\mu_a = \left[\frac{\partial A}{\partial N_a} \right]_{T, V, N_b, N_c} \quad (3-15)$$

$$\frac{\mu_a - \mu_a^\ominus}{kT} = \log \left(\frac{N_a kT}{p^\ominus V} \right) + \frac{v_o (N_b + N_c)}{V} \quad (3-16)$$

and similarly for μ_b and μ_c . The above equations will be more useful in terms of the reduced quantities introduced to discuss the penetrable-sphere model. We will add to that list a free-energy-density defined by

$$a = \frac{Av_o}{kTV} \quad (3-17)$$

and the definitions of the dimensionless activity becomes

$$\log z_\alpha = \frac{\mu_\alpha - \mu_\alpha^\ominus}{kT} + \log \pi^\ominus \quad (\alpha=a,b,c) \quad (3-18)$$

In terms of these quantities equations (3-12), (3-14) and (3-16) read

$$a = \sum_{\alpha=a,b,c} \rho_\alpha \left[\frac{\mu_\alpha^\ominus}{kT} + \log \left(\frac{\rho_\alpha}{\pi^\ominus} \right) - 1 \right] + \rho_a \rho_b + \rho_b \rho_c + \rho_c \rho_a \quad (3-19)$$

$$\pi = \rho_a + \rho_b + \rho_c + \rho_a \rho_b + \rho_b \rho_c + \rho_c \rho_a \quad (3-20)$$

$$\log z_a = \log \rho_a + \rho_b + \rho_c \quad (3-21)$$

and similarly for $\log z_b$ and $\log z_c$. Equations (3-19) to (3-21) are the basis of the following work.

We could have started alternatively with the Gibbs free energy as function of the compositions and temperature. It has a more complicated form but is well suited for numerical analysis [81]. The results are, naturally, identical and will be reviewed at the end of this chapter.

III.2 Equations for the critical phases

A critical phase in multicomponent mixtures is most simply determined by stability conditions. In all that follows we use the fact that the free energy surface is an analytic function everywhere.

According to stability theory [82] the Helmholtz free energy must be a convex function of density for a phase to be stable. When the curvature of the free energy surface changes sign a series of double- (or multiple-) tangent planes are possible, which means that there are regions where the free energy of the homogeneous system can be lowered by splitting into two (or more) phases [50a, 82]. The locus of contact points between the double-tangent plane and the free energy surface defines a boundary curve of coexisting states called the binodal (Figure 12, curve denoted ACB). It encloses a region where the homogeneous phase is unstable; there the free energy surface is concave-convex (a region of metastable equilibrium) or fully concave (absolutely unstable region). The locus of points which divide the concave-convex and the fully concave regions is the border of absolute instability and is called the spinodal (Figure 12, curve denoted DCE).

According to Gibbs [83] the critical phase is defined by the vanishing of all distinction between coexisting phases. Since there are always absolutely unstable states inside the binodal, it follows that the critical phase lies at the border between unstable and stable regions. Furthermore it is the point where the curvature of the free energy surface ceases to change sign, i.e. the surface is again fully convex. These two conditions define completely the critical phase according to the following theorem [82, 84]

Theorem: In a system of m independent components, a critical phase which does not coexist with other phases has $m-1$ degrees of freedom.

Corollary: For any number of components, the locus of a critical phase in phase space is determined by two equations.

For the binary mixture model which we are considering the critical phase (sometimes called plait-point) of species a and b is a single point (no degrees of freedom), not a line, since the configuration

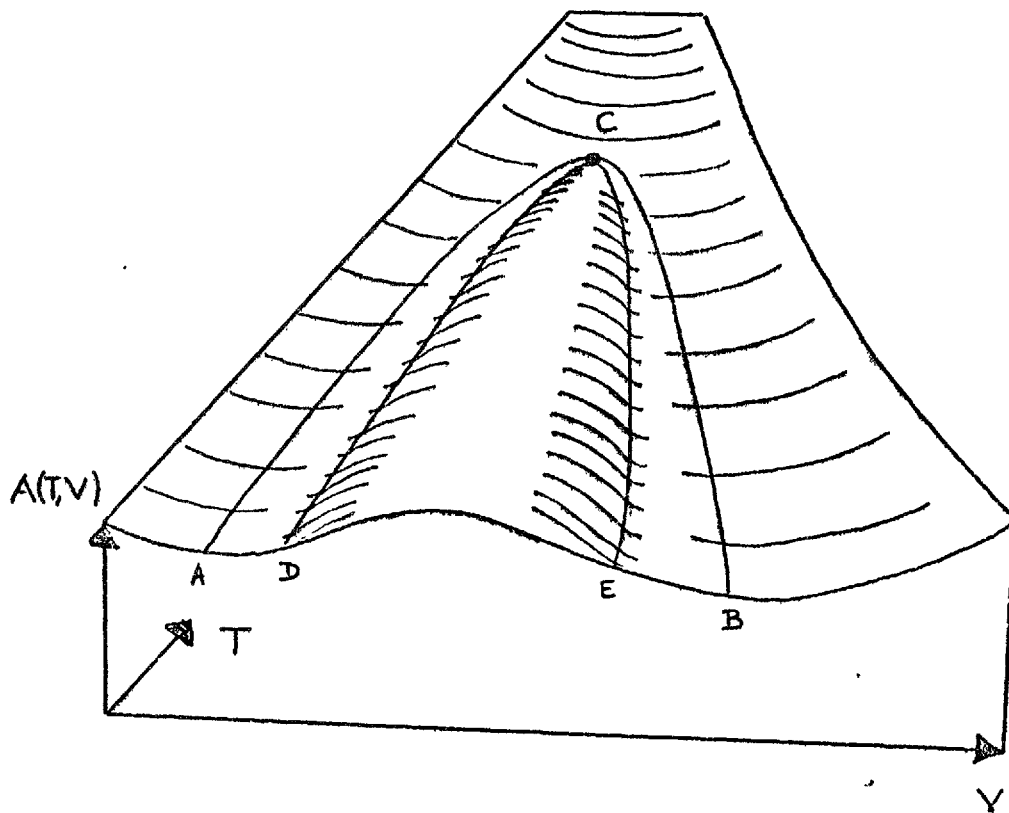


Figure 12 Free energy surface $A(T, V)$. The region where the single phase is unstable is shown; the curve ACB is the binodal, the curve DCB is the spinodal, both are tangent at the critical point, C .

energy is temperature-independent and consequently an additional degree of freedom is lost when the temperature (which is an irrelevant variable) is fixed. The critical pressure-to-temperature ratio, π , has then a fixed value. In the ternary mixture model the locus of such critical points define a line as π is varied, but another critical point (of higher order) is defined by the simultaneous vanishing of three phases. We will call the former a binary critical point or more shortly a bicritical point to distinguish it from the latter which is a tricritical point according to the terminology of Griffiths and Widom [66].

The mathematical formulation of these two conditions is also provided by the stability theory. Let us consider for simplicity a binary mixture. The first condition is expressed by the fact that the quadratic form $(\delta^2 a)$ should be positive definite at the spinodal [82] where a is the free energy density of eq. (3-19) and

$$\delta^2 a = \left[\frac{\partial^2 a}{\partial \rho_a^2} \right] (\delta \rho_a)^2 + \left[\frac{\partial^2 a}{\partial \rho_a \partial \rho_b} \right] \delta \rho_a \delta \rho_b + \left[\frac{\partial^2 a}{\partial \rho_b^2} \right] (\delta \rho_b)^2 \quad (3-22)$$

A necessary and sufficient condition for this to be so is that the determinant of the second derivatives of a vanishes, i.e.

$$D \equiv \begin{vmatrix} \frac{\partial^2 a}{\partial \rho_a^2} & \frac{\partial^2 a}{\partial \rho_a \partial \rho_b} \\ \frac{\partial^2 a}{\partial \rho_b \partial \rho_a} & \frac{\partial^2 a}{\partial \rho_b^2} \end{vmatrix} = 0 \quad (3-23)$$

This condition together with (3-20) at fixed π defines the spinodal and is the first equation for the critical point which is a point of this boundary. The second condition is obtained by noting that the variation (in the sense of a virtual displacement in Analytical Mechanics) of the critical phase cannot enter into the unstable region. This means that the variation of D , holding constant either $\left(\frac{\partial a}{\partial \rho_a} \right)$ or $\left(\frac{\partial a}{\partial \rho_b} \right)$, cannot be negative, that is

$$\delta D = \left[\frac{\partial D}{\partial \rho_a} \right] \delta \rho_a + \left[\frac{\partial D}{\partial \rho_b} \right] \delta \rho_b \geq 0 \quad (3-24)$$

If $\delta D > 0$ then by suitably reversing the signs of the independent variables (3-24) becomes negative; therefore it must be zero. Hence (3-24), as equality, must be satisfied simultaneously with either

$$\delta \left[\frac{\partial a}{\partial \rho_a} \right] = \left[\frac{\partial^2 a}{\partial \rho_a^2} \right] \delta \rho_a + \left[\frac{\partial^2 a}{\partial \rho_a \partial \rho_b} \right] \delta \rho_b = 0 \quad (3-25)$$

or

$$\delta \left[\frac{\partial a}{\partial \rho_b} \right] = \left[\frac{\partial^2 a}{\partial \rho_b \partial \rho_a} \right] \delta \rho_a + \left[\frac{\partial^2 a}{\partial \rho_b^2} \right] \delta \rho_b = 0 \quad (3-26)$$

This homogeneous system is satisfied if and only if the determinant

$$D' \equiv \begin{vmatrix} \frac{\partial^2 a}{\partial \rho_a^2} & \frac{\partial^2 a}{\partial \rho_a \partial \rho_b} \\ \frac{\partial^2 a}{\partial \rho_b \partial \rho_a} & \frac{\partial^2 a}{\partial \rho_b^2} \end{vmatrix} = 0 \quad (3-27)$$

(or with eq. (3-26)), vanishes. This condition is then the second one for the critical phase. The same procedure can be followed for any number of components and it is also a natural route to consider higher-order critical points [69, 82].

III.3 Binary systems

We will consider first the binary mixtures, since they are the limiting cases when the composition of one species is zero. We quote here only the main results as such mixtures have been studied in detail elsewhere [41].

The qualitative behaviour of the binary mixture is a fluid-fluid phase separation at high densities of both components. Since the potential between unlike species is that of hard spheres, the bicritical point occurs at fixed $\rho_a = \rho_b$, fixed p/T ratio and the critical line in the p, T space is the straight line $p = \text{const. } T$ for $x_a = x_b = \frac{1}{2}$.

When $\rho_c = 0$ the free energy of the mixture is

$$a = \sum_{\alpha=a,b} \rho_{\alpha} \left[\frac{\mu_{\alpha}}{kT} + \log \left(\frac{\rho_{\alpha}}{\pi} \right) - 1 \right] + \rho_a \rho_b \quad (3-28)$$

thus the equations for the bicritical point are

$$D = \begin{vmatrix} \rho_a^{-1} & 1 \\ 1 & \rho_b^{-1} \end{vmatrix} = \rho_a^{-1} \rho_b^{-1} - 1 \quad (3-29)$$

and

$$\begin{aligned} D' &= \begin{vmatrix} \rho_a^{-1} & 1 \\ -\rho_a^{-2} & \rho_b^{-1} \end{vmatrix} \\ &= -\rho_a^{-2} \rho_b^{-1} + \rho_a^{-1} \rho_b^{-2} \end{aligned} \quad (3.30)$$

or vice versa. Thus $D = 0$ and $D' = 0$ yield

$$\rho_a - 1 = 0$$

and

$$\rho_b - 1 = 0$$

(3-31)

The bicritical density is consequently $\rho_a = \rho_b = 1$. Substitution into (3-20) (with $\rho_c = 0$) gives

$$\pi^c = 3 \quad (3-32)$$

The spinodal is given by $D = 0$ or

$$\rho_a \rho_b = 1 \quad (3-33)$$

The binodal is obtained by equating the activities of both components and the pressure for each pair of conjugated states. Any particular tie-line is specified by fixing a value of π greater than 3 and solving the set

$$\begin{aligned} \log \rho_a' + \rho_b' &= \log \rho_a'' + \rho_b'' \\ \log \rho_b' + \rho_a' &= \log \rho_b'' + \rho_a'' \\ \rho_a' + \rho_b' + \rho_a' \rho_b' &= \rho_a'' + \rho_b'' + \rho_a'' \rho_b'' \end{aligned} \quad (3-34)$$

The three equations in the four unknowns ρ_a' , ρ_b' , ρ_a'' and ρ_b'' generate a boundary curve.

Symmetry allows us to simplify the set (3-34) if we note that

$$\begin{aligned} \rho_a' &= \rho_b'' \\ \rho_b' &= \rho_a'' \end{aligned} \quad (3-35)$$

since the two components play identical roles. Therefore (3-34) is reduced to the single equation between two unknowns

$$\log \rho_a' + \rho_b' = \log \rho_b' + \rho_a' \quad (3-36)$$

which has pairs of solutions for $\rho_a' > 1$, $\rho_b' < 1$ or vice versa. Table II shows selected values of ρ_a' and ρ_b' ; the phase diagram is depicted in Figures 13a and 13b.

III.4 Ternary system

As a third component is added the bicritical points are displaced from the sides of the coordinate triangle towards the centre. At low densities of the third component equilibria between two phases (a-rich and b-rich) persist and the symmetry of the phase boundary and spinodal is maintained. These curves form crescents developing from the sides of the coordinate triangle. The bicritical points march along the line of symmetry. (Figure 14).

The binodal is now generated by the equations

$$\begin{aligned} \log \rho_a' + \rho_b' + \rho_c' &= \log \rho_a'' + \rho_b'' + \rho_c'' \\ \log \rho_b' + \rho_c' + \rho_a' &= \log \rho_b'' + \rho_c'' + \rho_a'' \\ \log \rho_c' + \rho_a' + \rho_b' &= \log \rho_c'' + \rho_a'' + \rho_b'' \\ \rho_a' + \rho_b' + \rho_c' + \rho_a'\rho_b' + \rho_b'\rho_c' + \rho_c'\rho_a' &= \rho_a'' + \rho_b'' + \rho_c'' + \rho_a''\rho_b'' + \rho_b''\rho_c'' + \rho_c''\rho_a'' \end{aligned} \quad (3-37)$$

but as long as symmetry between the a-rich and b-rich phases persists the conditions

$$\begin{aligned} \rho_a' &= \rho_b'' \\ \rho_b' &= \rho_a'' \\ \rho_c' &= \rho_c'' \end{aligned} \quad (3-38)$$

allow us to simplify that set to the same single equation of the binary mixture binodal, namely

$$\log \rho_a' + \rho_b' = \log \rho_b' + \rho_a' \quad (3-39)$$

The spinodal is now obtained by the 3X3 determinant

π	BINODAL		SPINODAL	
	ρ_a	ρ_b	ρ_a	ρ_b
3,0	1,000000	1,000000	1,000000	1,000000
3,1	1,639190	0,553507	1,370156	0,729844
3,2	1,948649	0,424357	1,558258	0,641742
3,3	2,199813	0,343829	1,717891	0,582109
3,4	2,419541	0,286722	1,863325	0,536675
3,5	2,618722	0,243533	2,000000	0,500000
4,0	3,447484	0,124231	2,618034	0,381966
4,1	3,590115	0,110663	2,732044	0,366026
4,5	4,135251	0,071028	3,186141	0,315859
5,0	4,753982	0,042756	3,732051	0,267949
5,5	5,332454	0,026458	4,265564	0,234436
6,0	5,885472	0,016633	4,791288	0,208712

TABLE II DENSITY OF SPECIES
A,B,C ALONG THE BINODAL AND
SPINODAL OF THE BINARY MIX-
TURE MODEL.

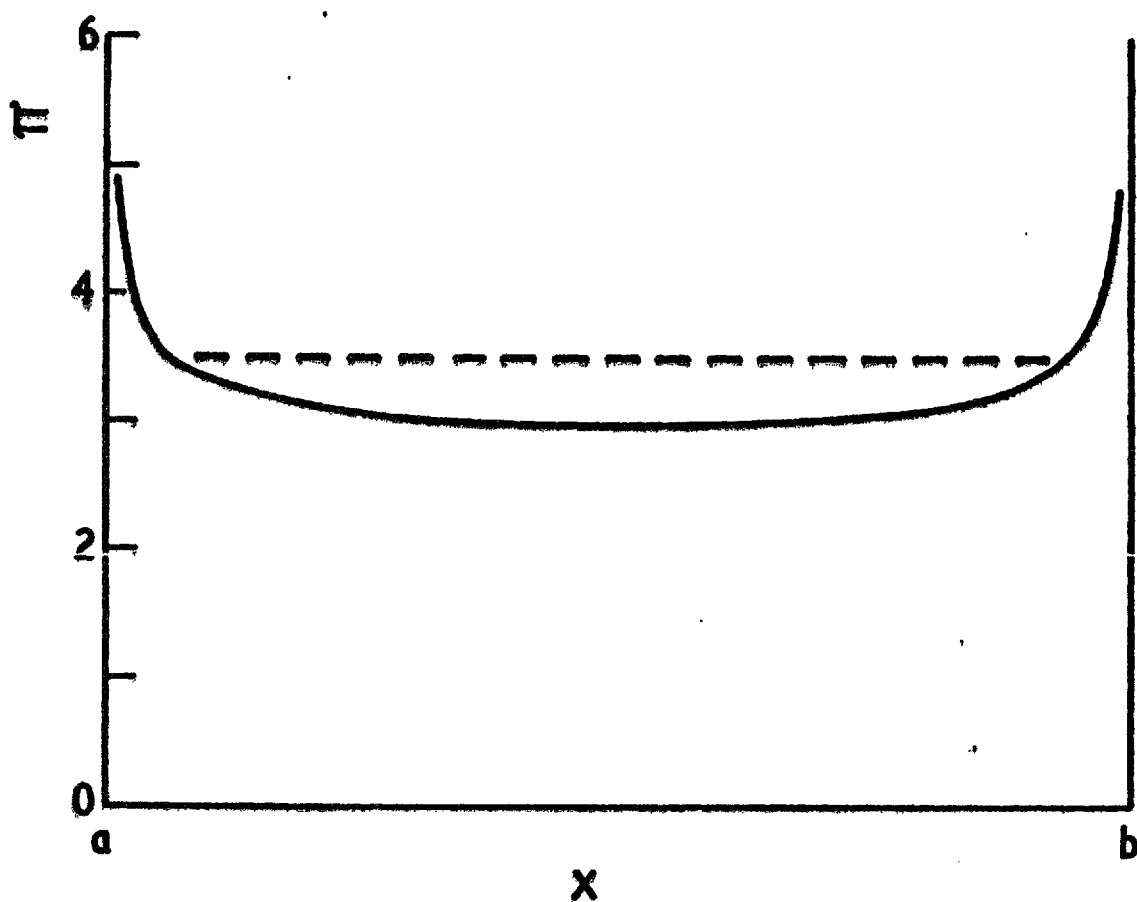


Figure 13 (a) Phase diagram of the binary mixture version of the penetrable-sphere model. By symmetry the critical point is at $x = \frac{1}{2}$.

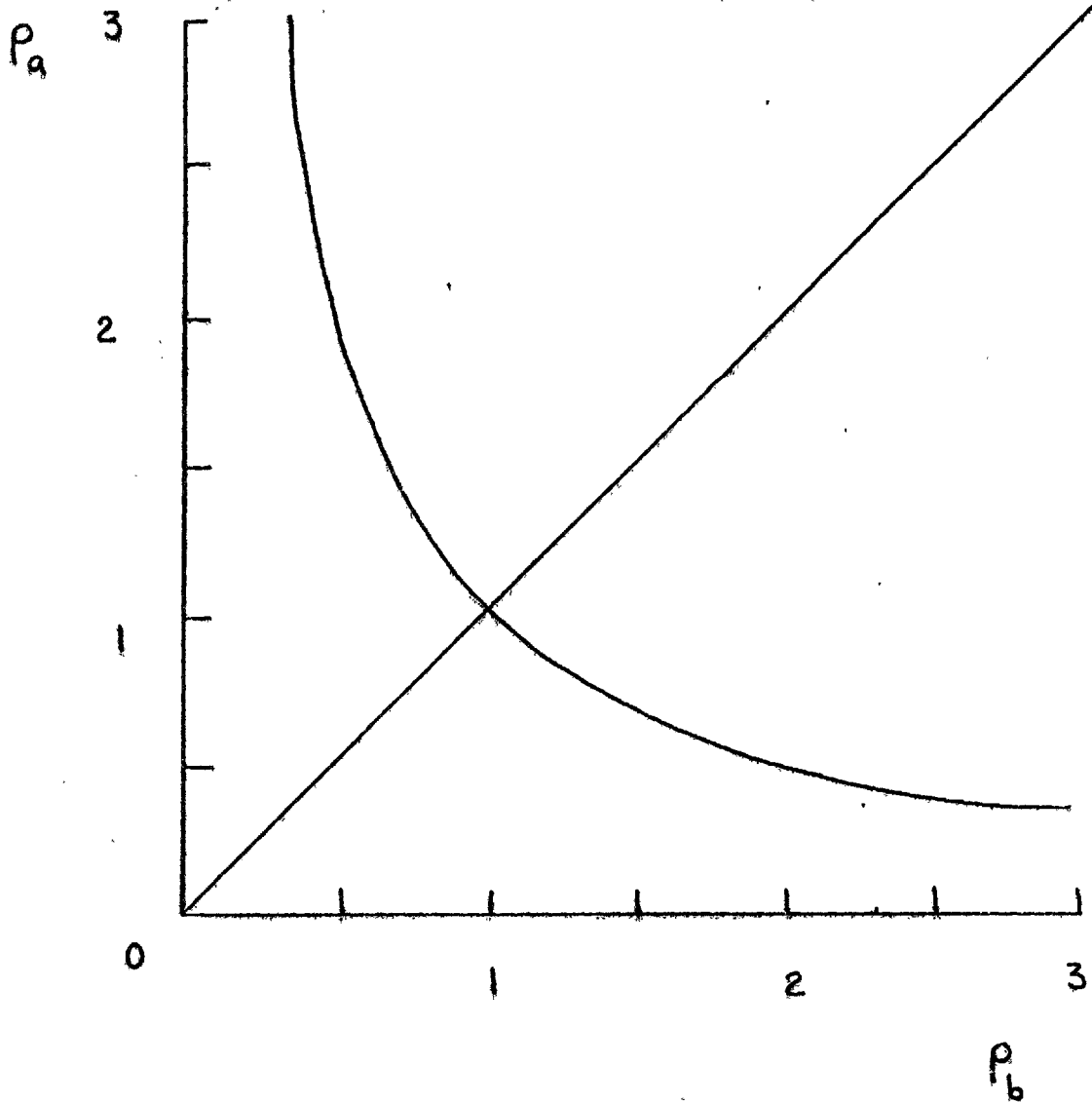


Figure 13 (b) Phase diagram of the binary mixture model. The symmetry between components a and b is explicit. The line $p_a = p_b$ is the line of symmetry.

$$D = \begin{vmatrix} \rho_a^{-1} & 1 & 1 \\ 1 & \rho_b^{-1} & 1 \\ 1 & 1 & \rho_c^{-1} \end{vmatrix} \quad (3-40)$$

$$= \frac{-1}{\rho_a} \frac{-1}{\rho_b} \frac{-1}{\rho_c} - \frac{-1}{\rho_a} - \frac{-1}{\rho_b} - \frac{-1}{\rho_c} + 2 \quad (3-41)$$

Setting $D = 0$ gives

$$2\rho_a\rho_b\rho_c - \rho_a\rho_b - \rho_b\rho_c - \rho_c\rho_a + 1 = 0 \quad (3-42)$$

The bicritical point at fixed π is defined by (3-42) and the curve $D' = 0$.

From (3-41)

$$\frac{\partial D}{\partial \rho_a} = -\rho_a^{-2} \rho_b^{-1} \rho_c^{-1} + \rho_a^{-2} \quad (3-43)$$

the other entries of D' are obtained from (3-43) by permuting cyclically ρ_a , ρ_b and ρ_c . After some algebra we have

$$\begin{aligned} D' = & -\rho_a^{-2} \rho_b^{-2} \rho_c^{-2} + 2\rho_a^{-2} \rho_b^{-2} \rho_c^{-1} + 2\rho_a^{-1} \rho_b^{-1} \rho_c^{-2} - \\ & -\rho_a^{-2} \rho_b^{-1} \rho_c^{-1} - \rho_a^{-1} \rho_b^{-2} \rho_c^{-1} - \rho_a^{-2} \rho_b^{-1} - \\ & -\rho_a^{-1} \rho_b^{-2} + \rho_a^{-2} + \rho_b^{-2} - \rho_c^{-2} \end{aligned} \quad (3-44)$$

Setting $D' = 0$ gives

$$\rho_c^2 [\rho_a(\rho_a - 1) + \rho_b(\rho_b - 1)] - \rho_c[(\rho_a - 1) + (\rho_b - 1)] - (\rho_a\rho_b - 1)^2 = 0 \quad (3-45)$$

and similarly by permuting ρ_a , ρ_b and ρ_c .

Equations (3-42) and (3-45) are satisfied for $\rho_a = 1$ and $\rho_b = 1$ irrespective the value of ρ_c , consequently the loci of bicritical points coincide with the line of symmetry. The displacement of the bicritical point as π is raised above 3 is given by

$$\begin{aligned}\rho_a &= 1 \\ \rho_b &= 1 \\ \rho_c &= \frac{\pi - 3}{3}\end{aligned}\tag{3-46}$$

III.5 Tricritical points

As π is raised beyond 3 the binodal and spinodal form crescents, the former enclosing completely the latter as required by thermodynamic stability. However, the system moves towards an unstable situation: the curvature near the maximum (point marked C in Figure 14) of the spinodal grows faster than that of the binodal until a pressure is reached when both are equal. For any higher pressure the spinodal improperly intersects the binodal, and although there is still a bicritical point at the expected position it lies inside an unstable region.

When the curvatures coincide any point near the maximum satisfies simultaneously the equations of both curves. Solving then eq. (3-42) for ρ_c and substituting that value in (3-20) gives

$$\rho_c = \frac{1 - \rho_a \rho_b}{\rho_a + \rho_b - 2\rho_a \rho_b}\tag{3-47}$$

$$\pi = 1 + \rho_a + \rho_b + \frac{(1 - \rho_a \rho_b)(1 + 2\rho_a \rho_b)}{\rho_a + \rho_b - 2\rho_a \rho_b}\tag{3-48}$$

For those points the densities ρ_a , ρ_b and ρ_c must also satisfy the equation for the binodal

$$\log(\rho_a/\rho_b) - \rho_a + \rho_b = 0\tag{3-49}$$

Let ρ_a and ρ_b very near the point $\rho_a = \rho_b = 1$ be given

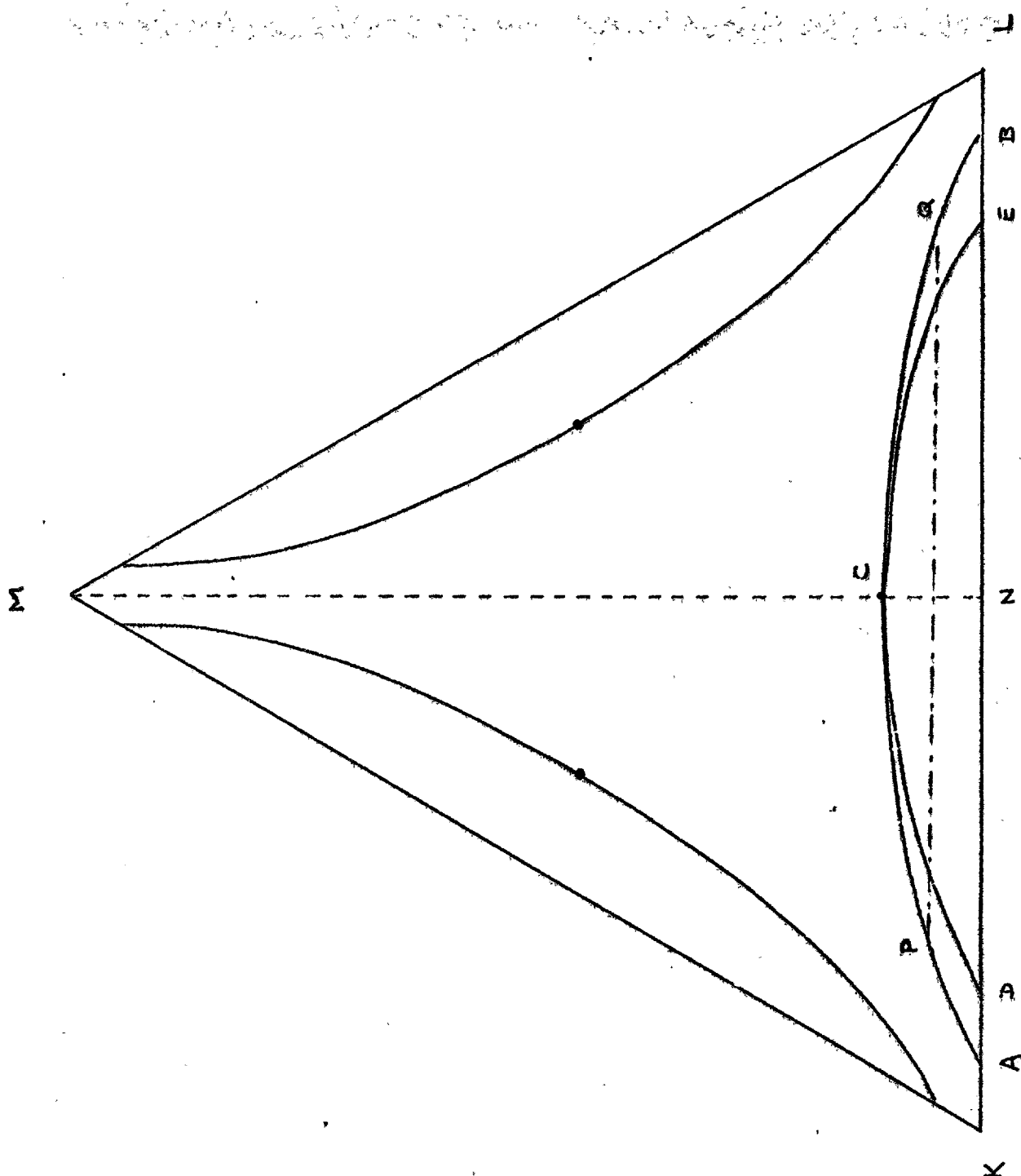


Figure 14 Phase diagram of the ternary mixture model. This is a three-fold symmetric system. The binodals form crescents ACB developing from the sides and enclosing the spinodals DCE; both boundaries are tangent at the bicritical point C, which lies on the line of symmetry MN. The tie-lines PQ are parallel to the sides. This symmetry is destroyed partially above the tricritical pressure.

$$\rho_a = 1 + \delta \quad (3-50)$$

$$\rho_b = 1 + \alpha\delta + \beta\delta^2 + o(\delta^3) \quad (3-51)$$

where $\delta \ll 1$. Expanding the logarithmic terms in (3-49) gives

$$\begin{aligned} (\rho_a - 1) - \frac{1}{2}(\rho_a - 1)^2 + \frac{1}{3}(\rho_a - 1)^3 + o(\rho_a^4) - \rho_a = \\ = (\rho_b - 1) - \frac{1}{2}(\rho_b - 1)^2 + \frac{1}{3}(\rho_b - 1)^3 + o(\rho_b^4) - \rho_b \end{aligned} \quad (3-52)$$

and using (3-50) and (3-51) this becomes

$$-\frac{1}{2}\delta^2 + \frac{1}{3}\delta^3 + o(\delta^4) = -\frac{1}{2}\alpha^2\delta^2 + (-\alpha\beta + \frac{1}{3}\alpha^3)\delta^3 + o(\delta^4) \quad (3-53)$$

Equating terms in the same power of δ

$$-\frac{1}{2} = -\frac{1}{2}\alpha^2 \quad (3-54)$$

$$\frac{1}{3} = -\alpha\beta + \frac{1}{3}\alpha^3 \quad (3-55)$$

from (3-54) $\alpha = \pm 1$; the positive sign is excluded since it leads to the trivial result $\rho_a = \rho_b$; with the negative sign we have $\beta = 2/3$, then

$$\rho_a = 1 + \delta \quad (3-56)$$

$$\rho_b = 1 - \delta + \frac{2}{3}\delta^2 + o(\delta^3). \quad (3-57)$$

Substituting (3-56) and (3-57) in (3-48) gives

$$\pi = 3 + \frac{2}{3}\delta^2 + \frac{\frac{1}{3}\delta^2(3 - \frac{2}{3}\delta^2)}{\frac{4}{3}\delta^2} \quad (3-58)$$

$$= \frac{15}{4} + \frac{2}{3} \delta^2 \quad (3-59)$$

and from (3-47)

$$\rho_c = \frac{1 - (1 + \delta)(1 - \delta + \frac{2}{3}\delta^2)}{2 + \frac{2}{3}\delta^2 - 2(1 + \delta)(1 - \delta + \frac{2}{3}\delta^2)} \quad (3-60)$$

$$= \frac{\frac{1}{4}\delta^2}{\frac{1}{3}\delta^2} = \frac{1}{4} \quad (3-61)$$

These values of π and ρ_c define the tricritical point. Table III shows some solutions of (3-47) to (3-49) near $\pi = 15/4$.

The point $\rho_a = \rho_b = 1$, $\rho_c = \frac{1}{4}$, $\pi = \frac{15}{4}$ is a tricritical point since on raising the pressure above $\pi = \frac{15}{4}$ three-phase equilibrium is developed. The coordinates of the three-phase triangle into which the tricritical point splits on raising π are obtained from the general equations for the pressure and the set of activities; by symmetry the apex lies on the line of symmetry and the two lower corners on the binodal.

A direct solution of the simultaneous equations obtained when the activities at the apex and lower corners are equated is not practicable since these equations vary slowly with density; an alternative procedure is followed.

Consider the activities of the three components along two paths, (i) the binodal and (ii) the line of symmetry. By conditions (3-38) $\log z_a = \log z_b$ along the binodal and, as $\rho_a = \rho_b$, also along the line of symmetry. Thus only the activities of two components are independent, let these be a and c . Plotting $\log z_a$ against $\log z_c$ on paths (i) and (ii) gives the intersecting lines of figure 15. (See following page). The physically meaningful part of (i) ends at D, the point where the binodal and spinodal cross, and of (ii) at C, the bicritical point. The intersection of (i) and (ii), E, is easily obtained by the secant method or any other modified Newton method [85]. In this way, the values of the activities at the vertices of the three-phase triangle are obtained. The densities of the coexisting states are obtained by back-solving for ρ_a , ρ_b and ρ_c the set

π	ρ_a	ρ_b	ρ_c
3,750	1,000000	1,000000	0,250000
3,755	1,109106	0,898296	0,249781
3,760	1,156457	0,858334	0,249630
3,765	1,193640	0,828528	0,249446
3,770	1,225558	0,803977	0,249261
3,775	1,254109	0,782780	0,249077
3,780	1,280265	0,763966	0,248894
3,785	1,304606	0,746956	0,248710
3,790	1,327510	0,731372	0,248527
3,795	1,349237	0,716954	0,248344
3,800	1,369978	0,703510	0,248161

TABLE III DENSITY OF SPECIES
A,B,C AT THE INTERSECTION OF
THE BINODAL WITH THE SPINODAL,

$$\log z_a^{(E)} = \log \rho_a + \rho_b + \rho_c$$

$$\log z_c^{(E)} = \log \rho_c + \rho_a + \rho_b \quad (3-62)$$

$$\pi = \rho_a + \rho_b + \rho_c + \rho_a \rho_b + \rho_b \rho_c + \rho_c \rho_a$$

on the binodal,

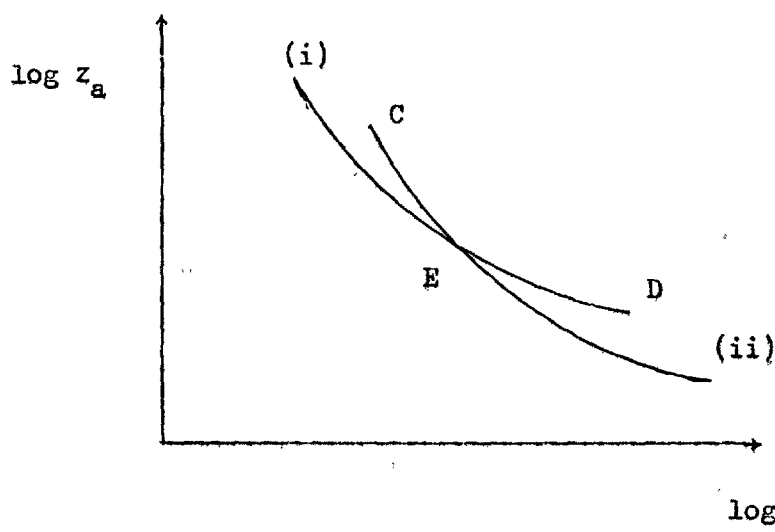


Figure 15 Activities of components a and c along the binodal (marked (i)) and the line of symmetry (marked (ii)).

and

$$\log z_a^{(E)} = \log \rho_a + \rho_a + \rho_c \quad (3-63)$$

$$\log z_c^{(E)} = \log \rho_c + 2\rho_a$$

on the line of symmetry, Specimen solutions are shown in Table IV. The last point is of special interest because four-phase equilibrium is exhibited at that pressure. This point is discussed in section III.10.

The tricritical point marks the bifurcation of the critical lines, defined by $D = 0$ and $D' = 0$. Specimen solutions are shown in Table V. For $\pi \leq 15/4$ the only solutions lie on the line of symmetry, but for $\pi > 15/4$ three solutions are found, one on the line of symmetry and two away. Figure 16 shows schematically the loci of bicritical points (note: this figure does not represent a constant- π plane). At $\pi = \frac{3}{2}(1 + \sqrt{3})$ the critical line crosses the line of symmetry other than that on which the tricritical point lies. This pressure is considered in more detail in section III.9.

π	LOWER CORNER			APEX	
	P_a	P_b	P_c	P_a	P_c
3,750	1,000000	1,000000	0,250000	1,000000	0,250000
3,760	1,200451	0,823211	0,247420	0,999989	0,253349
3,770	1,282952	0,762065	0,245414	0,999952	0,256739
3,780	1,347530	0,718074	0,243596	0,999886	0,260172
3,790	1,409839	0,678516	0,241244	0,999800	0,263635
3,800	1,464101	0,646176	0,239097	0,999687	0,267139
3,850	1,688709	0,530151	0,228612	0,998730	0,285267
3,900	1,873357	0,452370	0,218546	0,997098	0,304455
3,950	2,037255	0,393839	0,208841	0,994758	0,324782
4,000	2,187487	0,347371	0,199520	0,991666	0,346346
4,100	2,460644	0,277198	0,181942	0,983026	0,393657
4,200	2,708807	0,226269	0,165690	0,970657	0,447592
4,300	2,939324	0,187577	0,150658	0,953766	0,509985
4,400	3,156425	0,157284	0,136735	0,931045	0,583862
4,500	3,362905	0,133047	0,123805	0,900067	0,674877
4,627	3,613769	0,108559	0,108559	0,838817	0,838817

TABLE IV DENSITY OF SPECIES A,B,C
AT THE CORNERS OF THE THREE-PHASE
TRIANGLE, BY SYMMETRY THE OTHER
CORNER IS AT P_b, P_a, P_c

π	ρ_a	ρ_b	ρ_c
3.750	1.000000	1.000000	0.250000
3.755	1.083931	0.920510	0.250559
3.760	1.120080	0.888795	0.251124
3.765	1.148389	0.864914	0.251697
3.770	1.172650	0.845074	0.252277
3.775	1.194327	0.827810	0.252864
3.780	1.214172	0.812370	0.253458
3.785	1.232633	0.798306	0.254060
3.790	1.250000	0.785330	0.254670
3.795	1.266474	0.773238	0.255288
3.800	1.282201	0.761884	0.255914
3.850	1.414510	0.672796	0.262694
3.900	1.522762	0.606581	0.270657
3.950	1.618780	0.550867	0.280353
4.000	1.707107	0.500000	0.292893
4.025	1.749154	0.474859	0.300987
4.050	1.790058	0.448655	0.311286
4.075	1.829967	0.418927	0.326105
4.098	1.866025	0.366163	0.365888

TABLE V DENSITY OF SPECIES
A,B,C ALONG THE CRITICAL LINE.

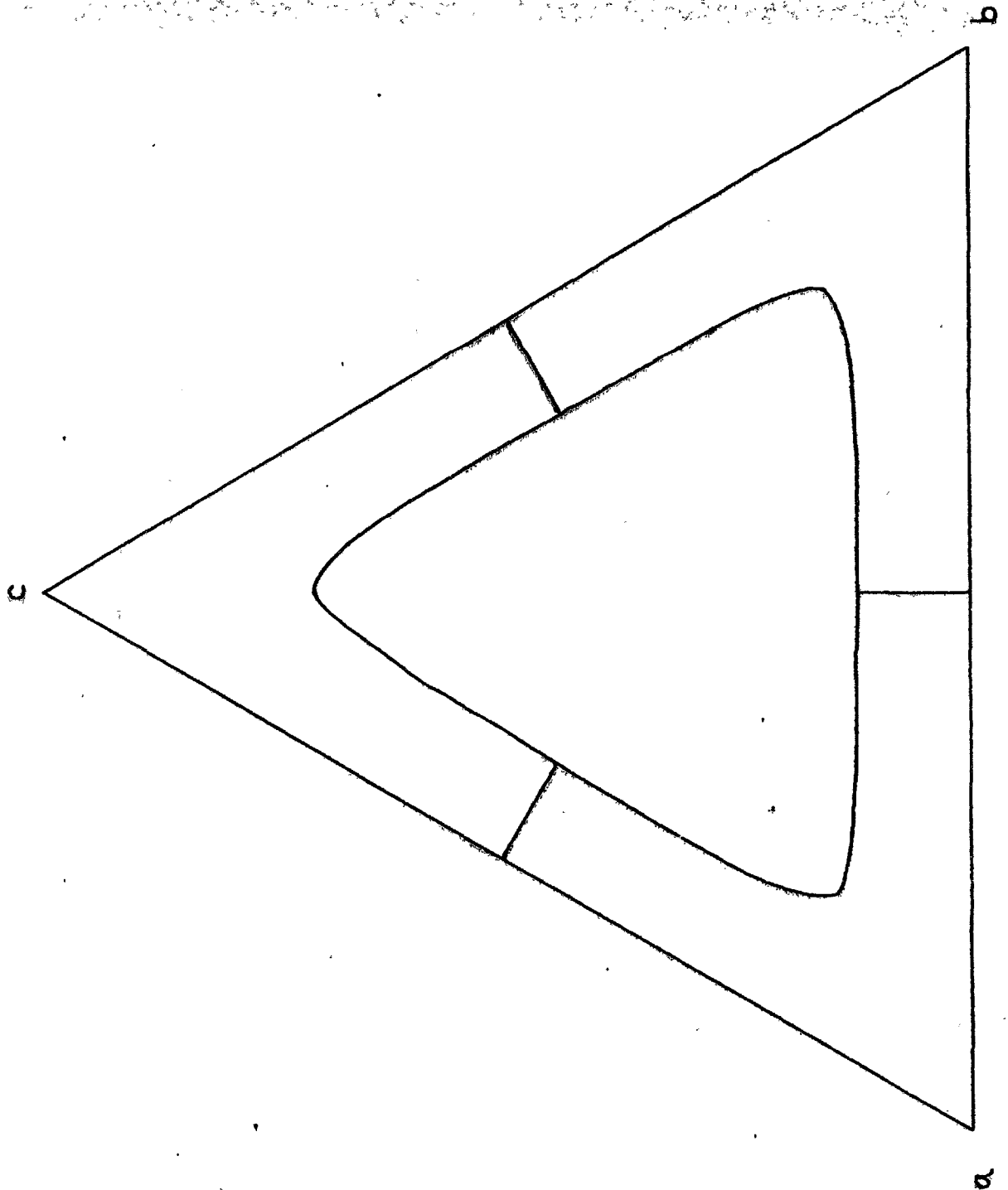


Figure 16 Loci of the bicritical points, or critical lines. The bifurcation corresponds to the tricritical point. This is not a constant-pressure plane,

The binodal undergoes some changes as well. Two secondary branches develop from the sides of the three-phase triangle, the base of which is the last tie-line of that part of the binodal symmetrical about $\rho_a = \rho_b$. The two secondary branches enclose completely the spinodal, which is tangent to both at two bicritical points corresponding to the solutions of $D = 0$ and $D' = 0$ away from the line of symmetry. Figures 17 and 18 show the phase diagram at the tricritical pressure, 3.75, and at $\pi = 3.80$ respectively. The geometry of the phase diagram is identical to that of the regular solutions of Meijering [50 b] as was pointed out in the introduction to this chapter.

III.6 Tricritical behaviour

The thermodynamic behaviour of the ternary mixture model in the vicinity of the tricritical point may be described by the vanishing of order parameters in the same way than in ordinary critical points. Four order parameters arise from the features described above, two related to the shape of the three-phase triangles and two to the bifurcation of the critical line.

The shape of the three-phase triangle has been described by the same order parameters as used by Griffiths [33] and Lang and Widom [70], namely the "base" and "height" of the triangle. The characteristic flatness of the triangles near the tricritical point is a distinctive feature of what was called "normal" diagrams in the introduction in contrast to the "anomalous" tricritical point (and phase-diagram) of Straley and Fisher [32]. Beyond all doubt the present model belongs to the class of "normal" tricritical point models. In the next two sections this assertion is justified by the values of the tricritical indices obtained. In the next chapter a more complete virial series is studied and the same conclusion is reached.

III.7 Shape of the three-phase triangle in the neighbourhood of the tricritical point

The point $\rho_a = \rho_b = 1, \rho_c = \frac{1}{4}$ at $\pi = 15/4$ is a tricritical point because three-phase equilibrium develops there. On raising the pressure a characteristic three-phase triangle is formed. Two tricritical exponents are defined to reflect this fact.

Let $(\rho_a', \rho_b', \rho_c')$ be the density of species, a, b and c at the apex and $(\rho_a'', \rho_b'', \rho_c'')$ at the lower corner. By symmetry the density of a, b

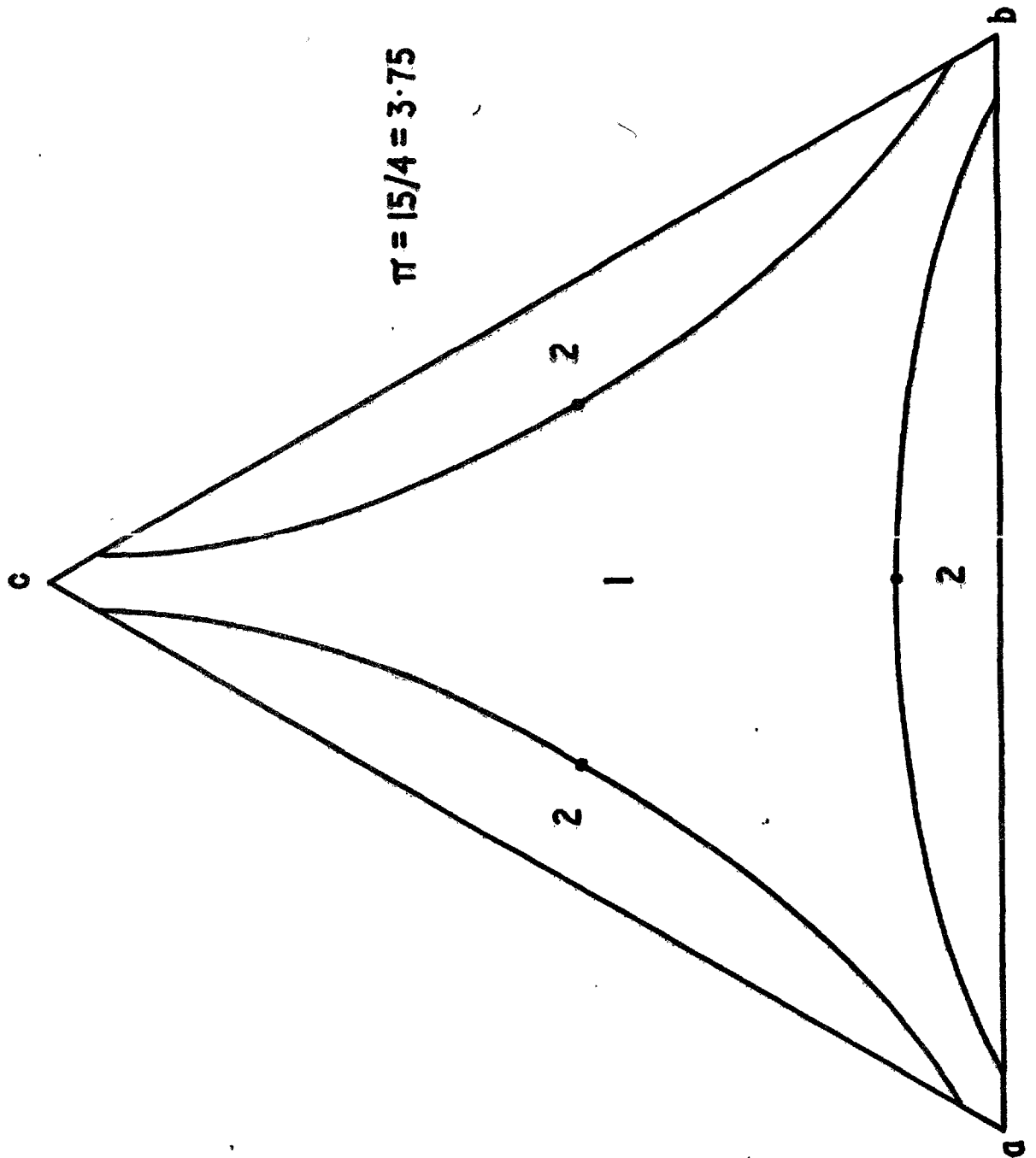


Figure 17 Phase diagram of the ternary mixture model at the tricritical pressure.

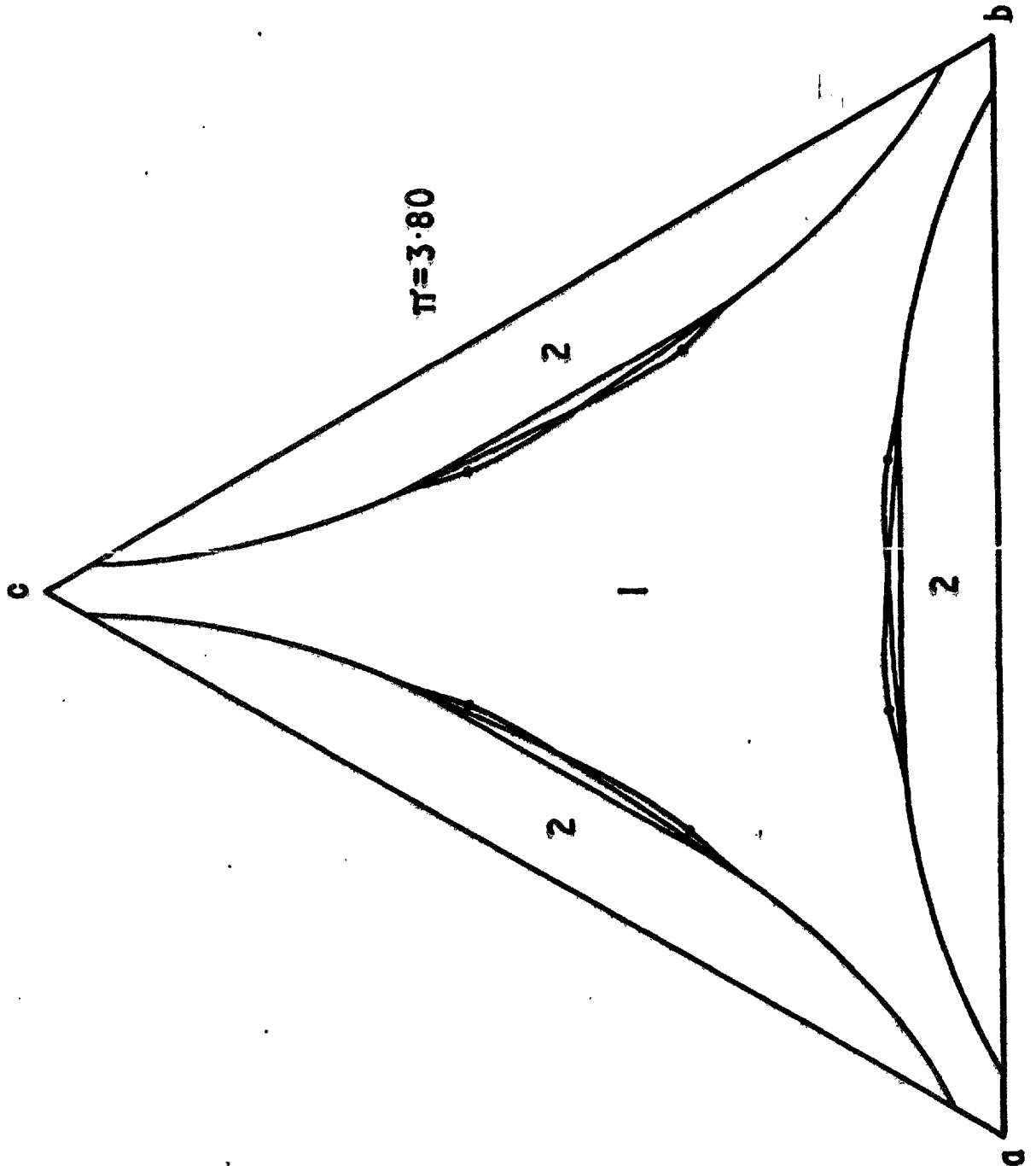


Figure 18 Phase diagram of the ternary mixture model
at $\pi = 3.80$

and c at the other corner is $(\rho_b'', \rho_a'', \rho_c'')$; thus we consider only half the triangle.

Let $\Delta h = \rho_c' - \rho_c''$ be the height of the triangle and $\Delta b = 2(\rho_a'' - \rho_b'')$ the length of the base, at a fixed pressure $\pi = 15/4$.

The tricritical exponents β_1 and β_2 are associated with the vanishing of the two characteristic dimensions of the three-phase triangles, as the tricritical pressure is approached, by the asymptotic laws

$$\Delta b \sim (\pi - \pi_{TC})^{\beta_1} \quad (3-64)$$

$$\Delta h \sim (\pi - \pi_{TC})^{\beta_2} \quad (3-65)$$

The exponents β_1 and β_2 corresponds to the notation of Lang and Widom [70].

In Figure 19 the height and base of three-phase triangles as function of pressure is shown. The former is a straight line and the latter is a parabola. Log-log plots of these curves produce the values $\beta_1 = \frac{1}{2}$, $\beta_2 = 1$ (Figure 20).

III.8 Critical lines

The other important feature near the tricritical point is the bifurcation of the critical lines, corresponding to the three solutions of $D = 0$ and $D' = 0$ above $\pi = 15/4$. We introduce two tricritical-point exponents to reflect this fact.

Let $(\rho_a^{TC}, \rho_c^{TC})$ be the critical densities of species a and c and $(\rho_a', \rho_b', \rho_c')$ be the density of a, b and c of one bicritical point on one of the stable branches of the critical line for $\pi > 15/4$.

Define two differences, d_{11} and d_1 , parallel and oblique to the line of symmetry, by

$$d_{11} = \rho_c' - \rho_c^{TC} \quad (3-66)$$

$$d_1 = \rho_a' - \rho_a^{TC} \quad (3-67)$$

and let θ_{11} and θ_1 be the tricritical exponents defined by the asymptotic laws

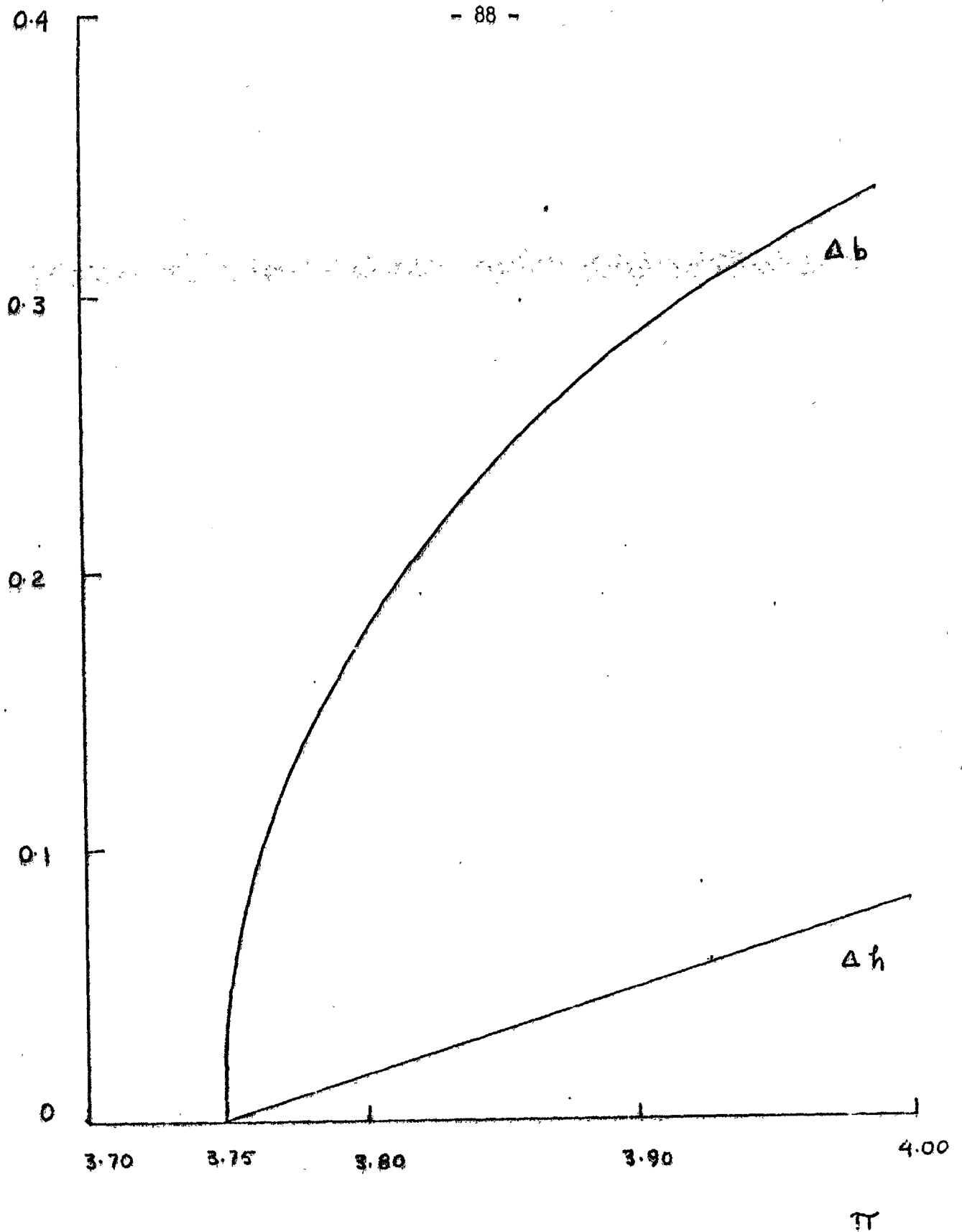


Figure 19 Shape of the three-phase triangles in the neighbourhood of the tricritical point. The base, Δb , is defined in eq. (3-64) and the height, Δh , in eq. (3-65) .

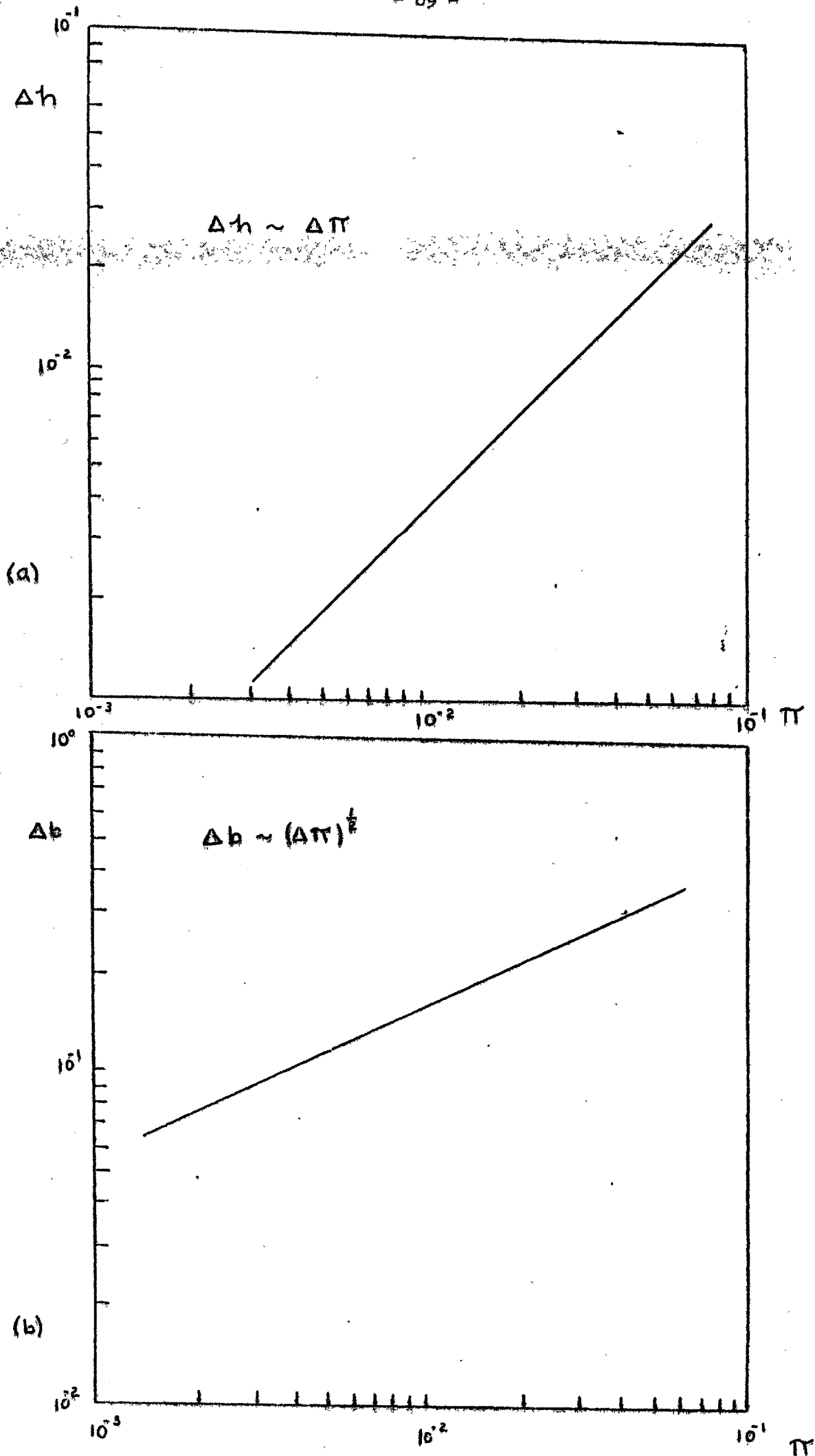


Figure 20 Tricritical exponents β_1 and β_2 .

$$d_{11} \sim (\pi - \pi^{TC})^{\theta_{11}} \quad (3-68)$$

$$d_1 \sim (\pi - \pi^{TC})^{\theta_1} \quad (3-69)$$

Figure 21 shows log-log plots of d_{11} and d_1 against $\Delta\pi = \pi - \pi^{TC}$. The values $\theta_{11} = 2$ and $\theta_1 = \frac{1}{2}$ are obtained from the limiting slopes.

III.9 Intermediate pressures

At higher pressures the three-phase triangles and the secondary branches of the binodal expand. The six bicritical points approach each other until they merge in pairs at the lines of symmetry. When this happens the spinodals cross.

Let π^+ be the pressure for this geometry. For $\pi < \pi^+$ the set of spinodals consists of three crescents developing from the sides of the coordinate triangle as in Figure 22a; for $\pi > \pi^+$ the set consists of three crescents now developing from the corners of the coordinate triangle and one closed branch surrounding the centre, as shown in Figure 22c. At $\pi = \pi^+$, thus, they must cross as shown in Figure 22b.

The condition for crossing is hence that a line of symmetry changes from cutting the spinodals only once ($\pi < \pi^+$) to cutting them three times ($\pi > \pi^+$).

Consider the line of symmetry $\rho_a = \rho_b$ and call

$$\rho_a = \rho_b = x \quad (3-70)$$

Equation (3-42) gives

$$\rho_c = \frac{1+x}{2x} \quad (3-71)$$

and the equation for the pressure becomes a cubic in the common value of ρ_a and ρ_b :

$$x^3 + 3x^2 - (\pi - \frac{3}{2})x + \frac{1}{2} = 0 \quad (3-72)$$

This equation has one real root if

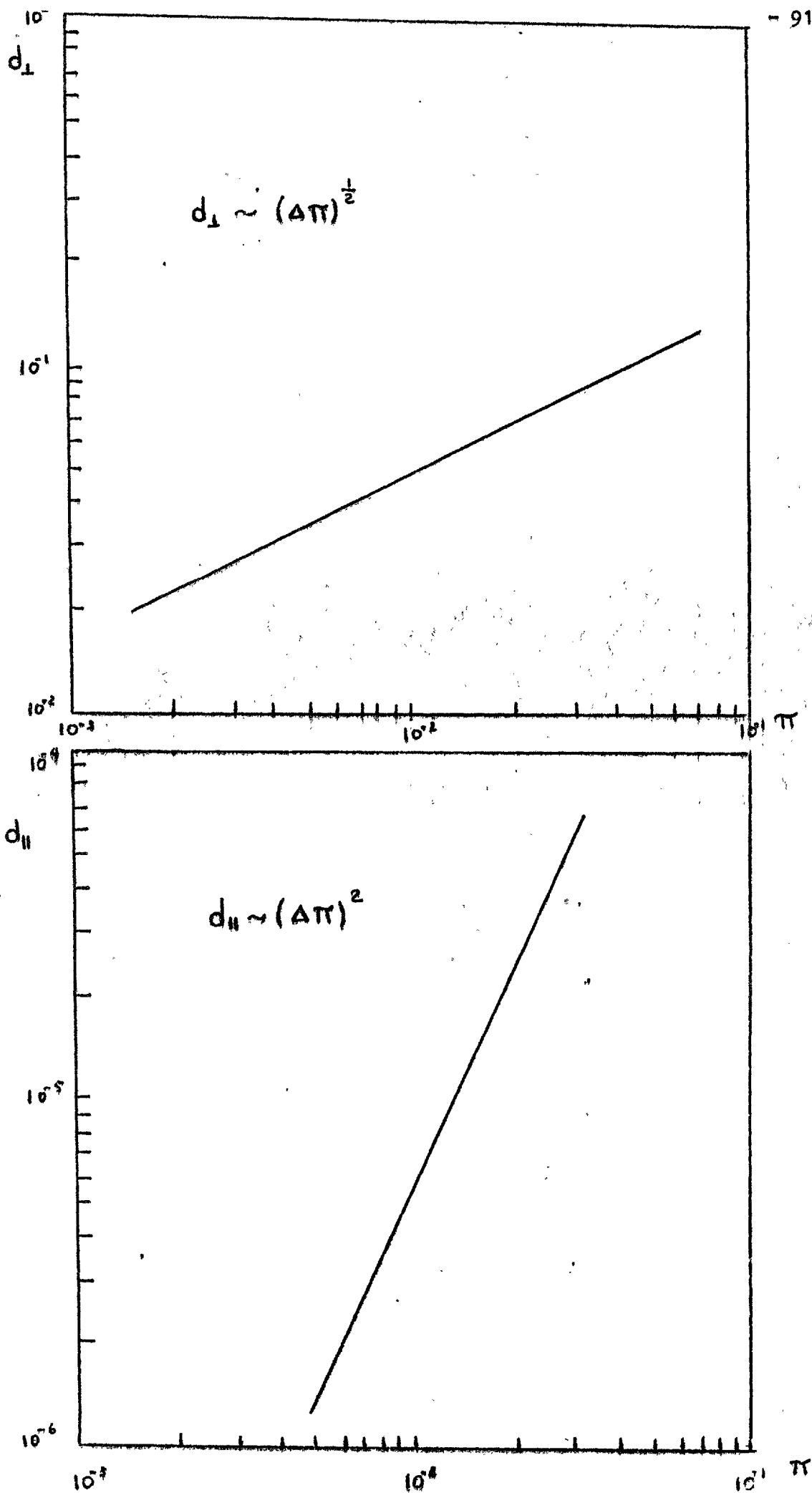
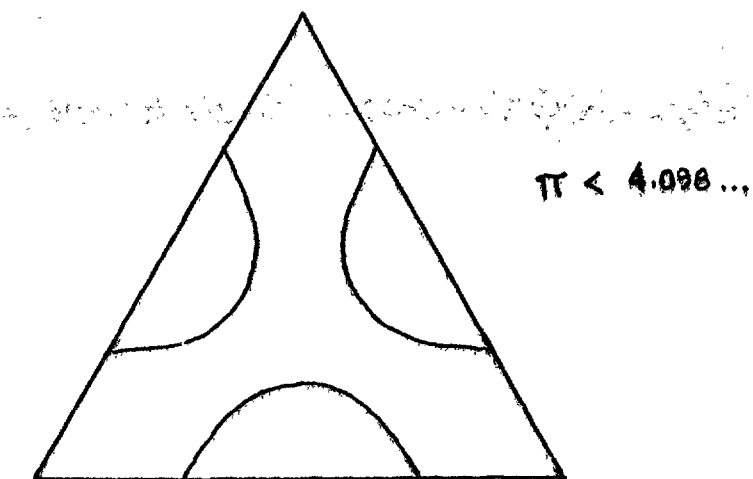
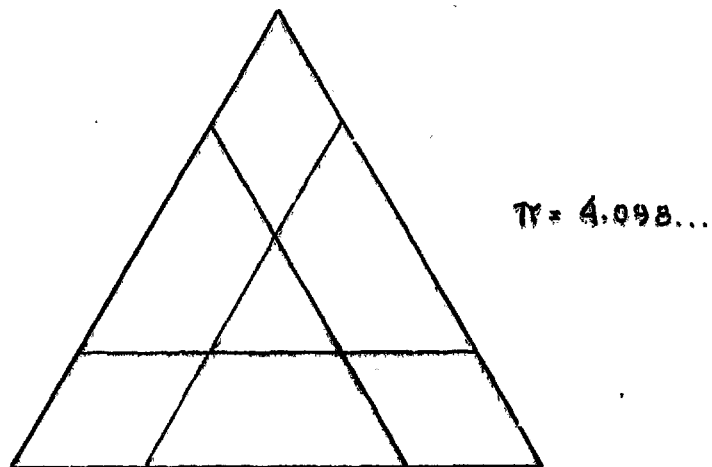


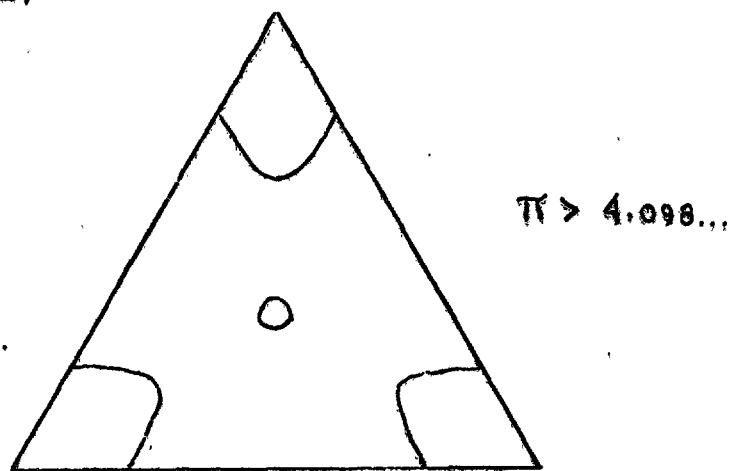
Figure 21 Tricritical exponents $\theta_{\parallel}$ and $\theta_{\perp}$.



(a)



(b)



(c)

Figure 22 The spinodals near $\pi = 4.098 \dots$

$$27(\pi + 1)^2 > 4(\pi + \frac{3}{2})^3 \quad (3-73)$$

and three otherwise [86] . The pressure π^+ is then the solution of (3-73) as equality:

$$\pi^+ = \frac{3}{2} (1 + \sqrt{3}) = 4.0980762... \quad (3-74)$$

Substitution of (3-74) in (3-72) gives

$$\rho_a = \rho_b = \frac{1}{2} (\sqrt{3} - 1) = 0.366025... \quad (3-75)$$

and (3-71) gives

$$\rho_c = \frac{1}{2} (2 + \sqrt{3}) = 1.866025... \quad (3-76)$$

The phase diagram at $\pi = 4.098...$ is shown in Figure 23.

III.10 High pressure: quadruple point

When the pressure is further increased beyond the point at which the six bicritical points have merged in pairs the binary regions enclosed by the secondary branches of the binodals join forming strips connecting two by two the sides of the three-phase triangles (Figure 24). The triangles themselves expand, the apex moving towards the centre and the lower corners toward the lines of symmetry other than that on which the apex lies. When the three apices merge at the centre the six lower corners reach the lines of symmetry that they are approaching. Four-phase equilibria between an equimolar and a-rich, b-rich and c-rich phases is then established (Fig.25).

The computation of the densities of coexisting states is greatly simplified by the symmetry of this particular point; at the centre all three components have the same density,

$$\rho_a = \rho_b = \rho_c = x \quad (\text{centre}) \quad (3-77)$$

The equation for the pressure becomes

$$3x^2 + 3x - \pi = 0 \quad (3-78)$$

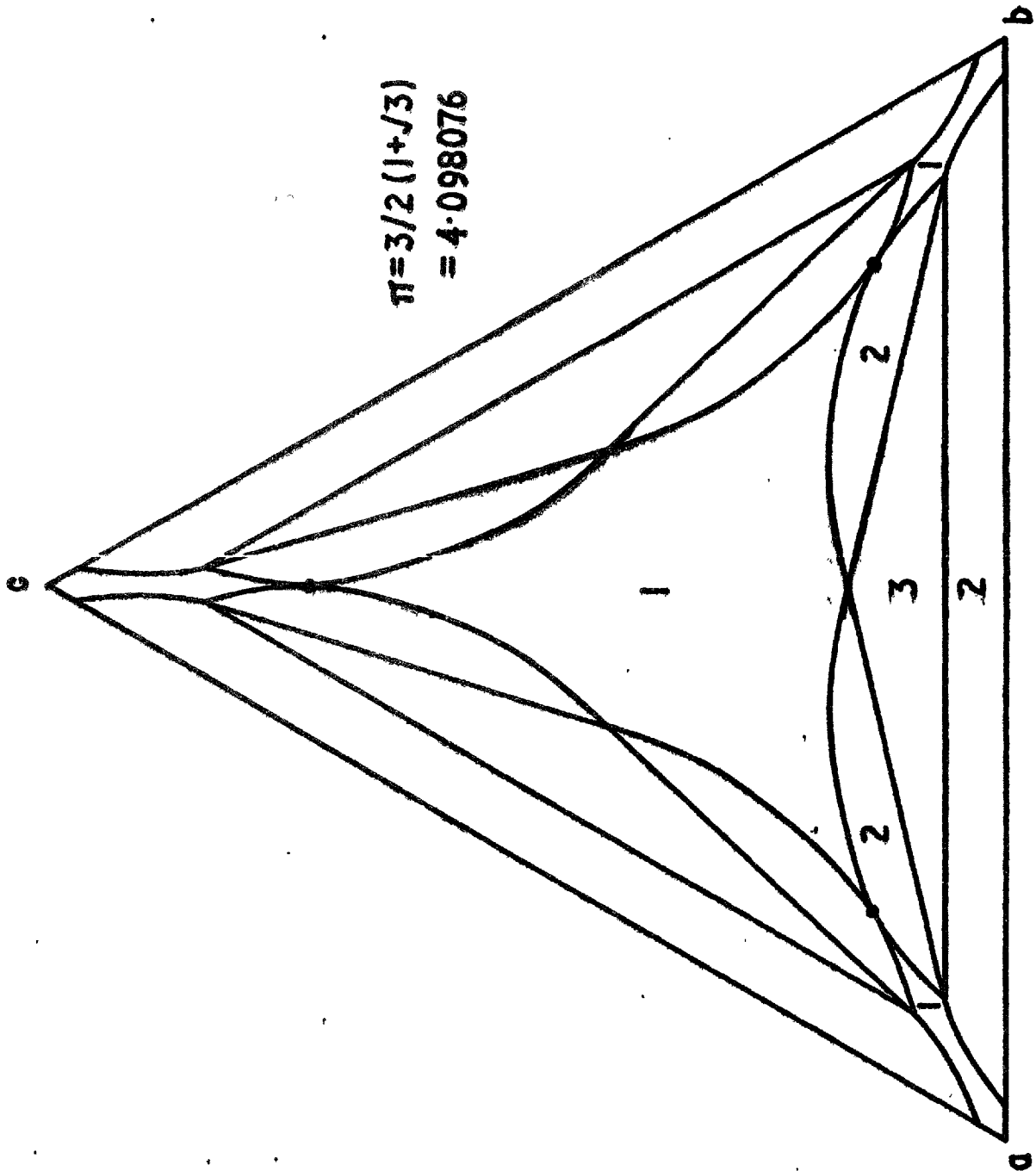


Figure 23 Phase diagram of the ternary mixture model at $\pi = 4.098, \dots$

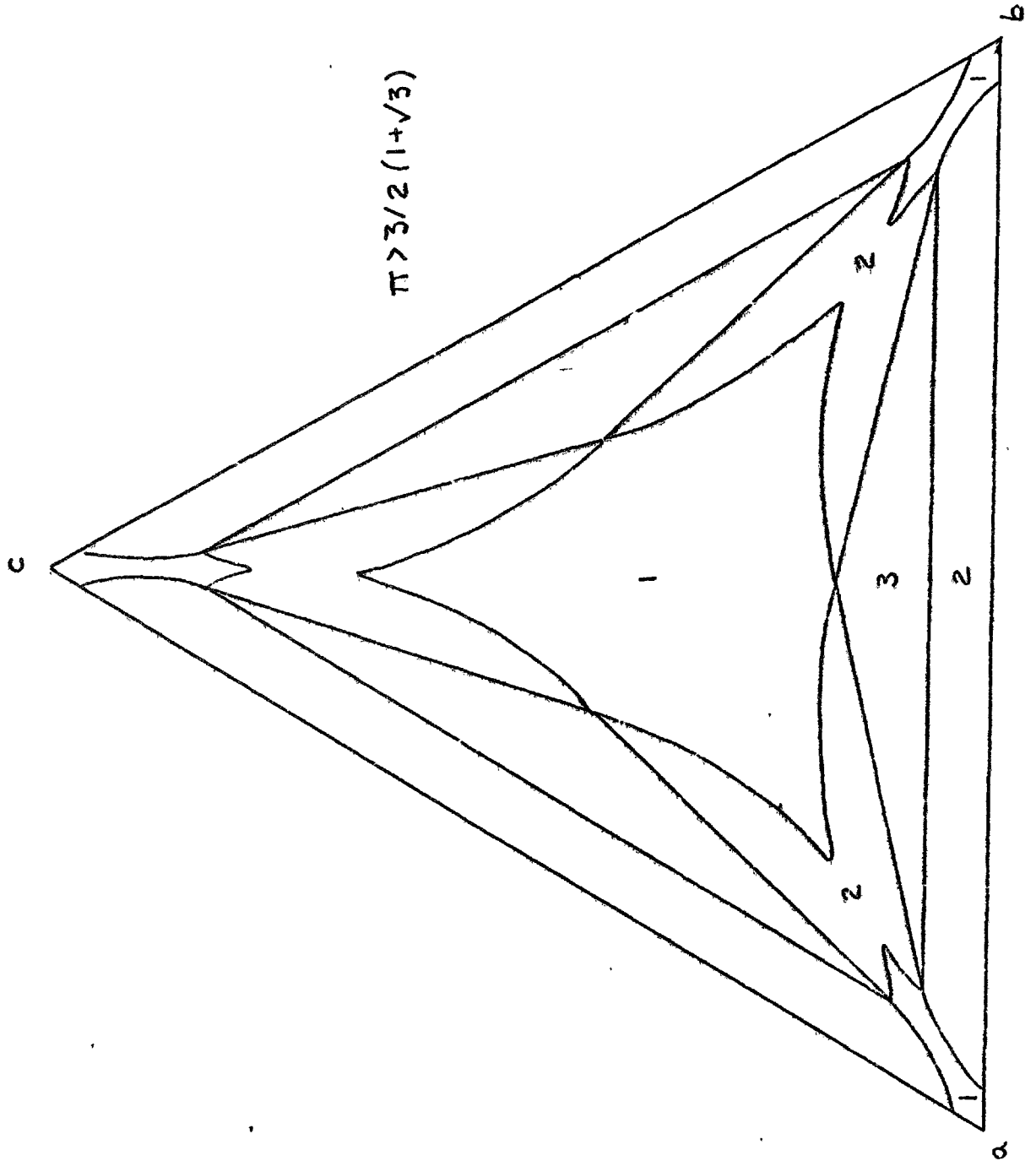


Figure 24 Phase diagram of the ternary mixture model in the pressure range $4.098 \leq \pi \leq 4.627$

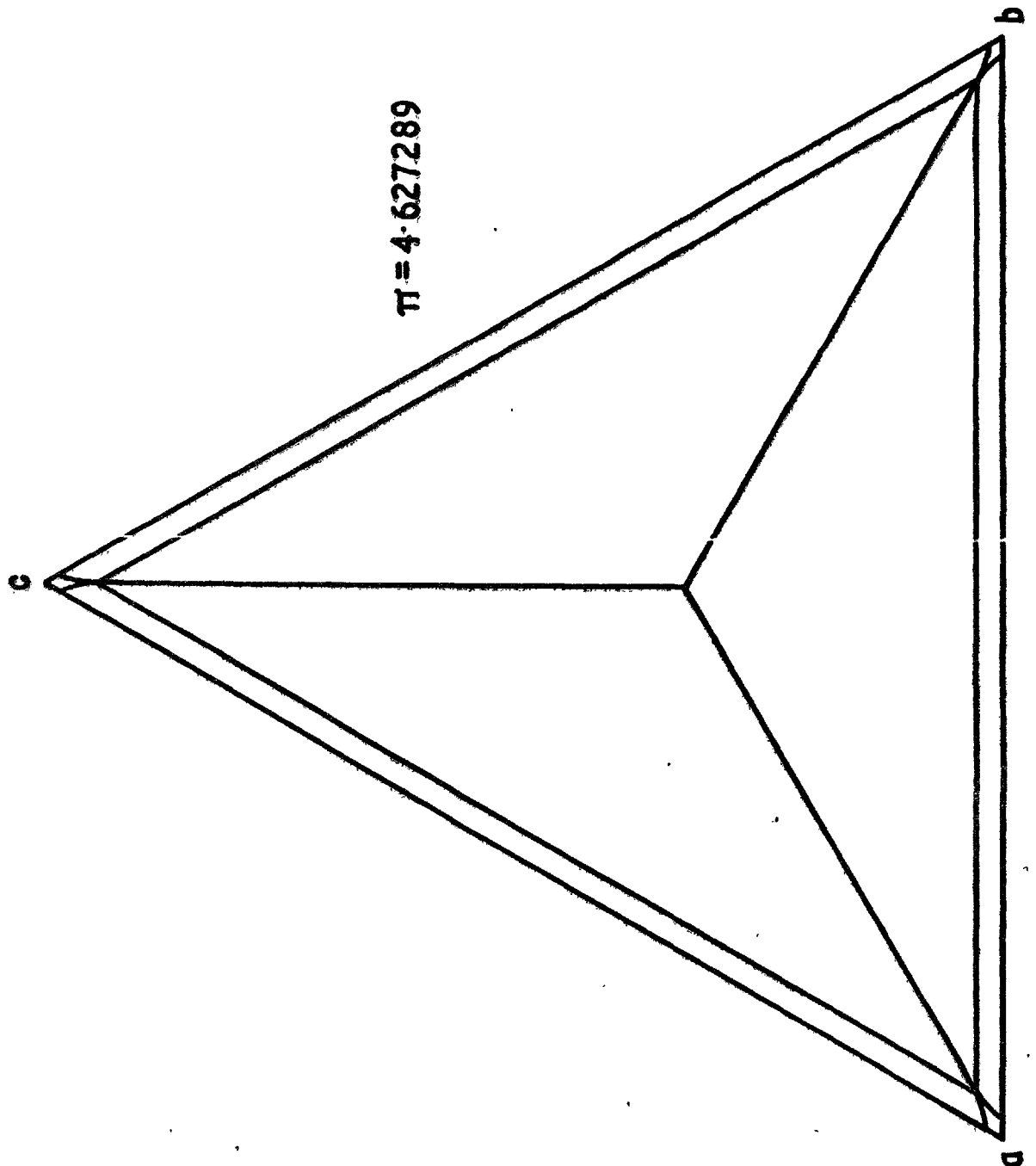


Figure 25 Phase diagram of the ternary mixture model
at the quadruple-point pressure.

At the lower corners two densities are equal and the third is obtained from the pressure equation

$$\rho_b = \rho_c = y \quad (\text{lower corner}) \quad (3-79)$$

$$\rho_a = \frac{\pi - 2y - y^2}{1 + 2y}$$

On equating the activities at the apex and the lower corner gives

$$\log \left(\frac{\pi - 2y - y^2}{1 + 2y} \right) + 2y = \log x + 2x \quad (3-80)$$

$$\log y + y + \left(\frac{\pi - 2y - y^2}{1 + 2y} \right) = \log x + 2x \quad (3-81)$$

Equations (3-78), (3-80) and (3-81) define the values of x, y and π . The solution is

$$\rho_a = 3.613769 \quad (\text{lower corner}) \quad (3-82)$$

$$\rho_b = \rho_c = 0.108559$$

$$\rho_a = \rho_b = \rho_c = 0.838817 \quad (\text{centre}) \quad (3-83)$$

at the quadruple-point pressure

$$\pi = 4.627289 \quad (3-84)$$

For still higher pressures the centre becomes unstable with respect to the corners and a single three-phase region forms in the middle. Table VI shows some states in the neighbourhood of the quadruple point. For $\pi < 4.627\dots$ the "lower corner" has not really that meaning, but is the point where the binodal cuts the line of symmetry; this point lies in the unstable portion of the binodal which runs inside the spinodal, nevertheless this range of pressures is shown for reference.

T	DENSITIES			CHEMICAL POTENTIALS	
	CENTRE	LOWER CORNER		CENTRE	LOWER CORNER
4,5	0,822876	3,206904	0,150978	1,450801	1,467262
4,6	0,835415	3,540591	0,115198	1,491003	1,494691
4,627	0,838817	3,613768	0,108559	1,501870	1,501870
4,7	0,847838	3,789562	0,094119	1,530610	1,520489
4,8	0,860147	4,001222	0,079231	1,569642	1,545061
4,9	0,872346	4,190620	0,067889	1,608123	1,568627
5,0	0,884437	4,364870	0,058870	1,646071	1,591329
5,2	0,908309	4,682539	0,045350	1,720446	1,634540
5,4	0,931782	4,972375	0,035694	1,792908	1,675285
5,6	0,954877	5,243327	0,028499	1,863581	1,713955
5,8	0,977611	5,500589	0,022989	1,932578	1,750853
6,0	1,000000	5,747501	0,018685	2,000000	1,786135

TABLE VI DENSITIES AND CHEMICAL POTENTIALS OF STATES AT THE INTERSECTION OF THE BINODAL WITH THE LINE OF SYMMETRY (LOWER CORNER) AND THE CENTRE OF THE COORDINATE TRIANGLE.

The binodals first cut the line of symmetry at $\pi = 4.438\dots$, which is the minimum value of π for which the equation.

$$\log \left| \frac{\pi - 2y - y^2}{y(1 + 2y)} \right| - \frac{\pi - 3y - 3y^2}{1 + 2y} = 0 \quad (3-85)$$

(where y is the common value of ρ_b and ρ_c defined in eq.(3-79)) has a solution with $0 < y < 1$. For $\pi \geq 4.627$ the lower corner is that of the three-phase region. From Table VI it is clear that the only equilibrium point is the quadruple, where the activities at the centre and lower corner are equal.

III.11 The Gibbs free energy

An entirely similar picture of the one described above is obtained starting from the Gibbs instead of the Helmholtz free energy. The results outlined in this section were communicated privately [81] and obtained independently of the work above.

The equation of state is

$$\frac{pV}{RT} = 1 + \frac{B}{V} \quad (3-86)$$

where

$$B = 2B^* (x_1x_2 + x_2x_3 + x_3x_1) \quad (3-87)$$

x_1 , x_2 and x_3 are the mol fractions of components a, b and c ($x_i = N_i / (N_a + N_b + N_c)$) and B^* is the molar second virial coefficient related to the molecular virial coefficient of eq. (3-7) by

$$B^* = N B_{ab} \quad (3-88)$$

where N is Avogadro's number.

Instead of the pressure-to-temperature ratio it is more convenient

to use its reciprocal,

$$\frac{RT}{B p} = \frac{2}{\pi} \quad (3-89)$$

x_2 and x_3 are arbitrarily chosen as the independent compositions, then

$$x_1 = 1 - x_2 - x_3 \quad (3-90)$$

A) Binary mixture

The binary mixture is exactly soluble because of the symmetry. the binodal, defined by $\left(\frac{\partial g_m}{\partial x_2} \right) = 0$ is

$$\left. \frac{RT}{B p} \right|_{\text{binodal}} = 2 \left\{ \frac{L^2(x_2)}{(x_2 - x_2^2) - L(x_2)} \right\} \quad (3-91)$$

where

$$L(x_2) = \frac{1 - 2x_2}{\log \left(\frac{1 - x_2}{x_2} \right) - \frac{1 - 2x_2}{x_2 - x_2^2}} \quad (3-92)$$

and the spinodal is

$$\left. \frac{RT}{B p} \right|_{\text{spinodal}} = \frac{2}{1 + \left\{ \frac{1}{(x_2 - x_2^2)^2} \right\}} \quad (3-93)$$

The bicritical point occurs at $x_2 = \frac{1}{2}$ at the critical temperature

$$\frac{RT}{B^* p} = \frac{2}{3} \quad (3-94)$$

that is, $\pi = 3$,

B) The ternary mixture

For the ternary mixture the Gibbs free energy assumes a complicated expression

$$\begin{aligned} g_m = g^\ominus + RT \left\{ \sum_{\alpha=1}^3 x_\alpha \log x_\alpha + \log \left[\frac{RT}{4B^* p} \right] - \right. \\ \left. - \log (x_1 x_2 + x_2 x_3 + x_3 x_1) + \log \left[\left(1 + \frac{8B^* p}{RT} (x_1 x_2 + x_2 x_3 + x_3 x_1) \right)^{\frac{1}{2}} - 1 \right] \right. \\ \left. + \left[\left(1 + \frac{8B^* p}{RT} (x_1 x_2 + x_2 x_3 + x_3 x_1) \right)^{\frac{1}{2}} - 1 \right] \right\} \end{aligned} \quad (3-95)$$

where $g^\ominus$ refers to a standard state.

The spinodal is given by $D = 0$, where D is

$$D = \begin{vmatrix} \frac{\partial^2 g_m}{\partial x_2^2} & \frac{\partial^2 g_m}{\partial x_2 \partial x_3} \\ \frac{\partial^2 g_m}{\partial x_3 \partial x_2} & \frac{\partial^2 g_m}{\partial x_3^2} \end{vmatrix} \quad (3-96)$$

There are two solutions along the line of symmetry; one is

$$\frac{RT}{B_p} = \frac{2x_2}{3(1-x_2)} \quad 0 \leq x_2 \leq 1 \quad (3-97)$$

which springs from the bicritical point; the other is more complicated and has a maximum at

$$\frac{RT}{B_p} = 0.488035$$

and (3-98)

$$x_2 = x_3 = 0.140883$$

The latter corresponds to the intersection of the spinodal curves at the lines of symmetry described in section III.9.

Symmetry shows that (3-97) and (3-98) also satisfy the condition $D' = 0$, where

$$D' = \begin{vmatrix} \frac{\partial D}{\partial x_2} & \frac{\partial D}{\partial x_3} \\ \frac{\partial^2 g_m}{\partial x_2 \partial x_3} & \frac{\partial^2 g_m}{\partial x_3^2} \end{vmatrix} \quad (3-99)$$

because $\frac{\partial D}{\partial x_2}$ is always zero along the line $x_1 = x_2$.

Equation (3-97) satisfies (3-99) when $\frac{\partial^2 g_m}{\partial x_2 \partial x_3} = 0$; the point (3-98)

satisfies it because $\frac{\partial D}{\partial x_3}$ is zero there. Therefore (3-97) is a locus of bicritical points (or critical lines).

The binodal is the locus of points for which

$$\left(\frac{\partial g_m}{\partial x_2} \right)_{x_3} = 0 \quad (3-100)$$

where $\left[\frac{\partial g_m}{\partial x_3} \right]$ is symmetric about $x_1 = x_2$. This binodal is found by solving iteratively the equation

$$\frac{RT}{B p} = 2 \left\{ \frac{L^2(x_2, x_3)}{x_2 + x_3 - x_2^2 - x_3^2 - x_2 x_3 - L(x_2, x_3)} \right\} \quad (3-101)$$

where

$$L(x_2, x_3) = \frac{1 - 2x_2 - x_3}{\log \left[\frac{1 - x_2 - x_3}{x_2} \right] + \frac{1 - 2x_2 - x_3}{x_2 + x_3 - x_2^2 - x_3^2 - x_2 x_3}} \quad (3-102)$$

In the temperature range

$$\frac{2}{3} \geq \frac{RT}{B p} \geq \frac{8}{15} \quad (3-103)$$

$\left(\frac{\partial g_m}{\partial x_3} \right)$ varies monotonically along the binodal, this means that in this range the phase diagram is simply a set of two phase regions as shown in Figure 17; the tie-lines are parallel to the side of the triangle and the bicritical points are described by (3-97).

For lower temperature $\left(\frac{\partial g_m}{\partial x_3} \right)$ no longer varies monotonically because a third phase begins to coexist with the other two on the line of symmetry. The point

$$\frac{RT}{B p} = \frac{8}{15} \quad (3-104)$$

($\pi = 15/4$) is then a tricritical point. The corners of the three-phase triangle into which the tricritical point splits are found by

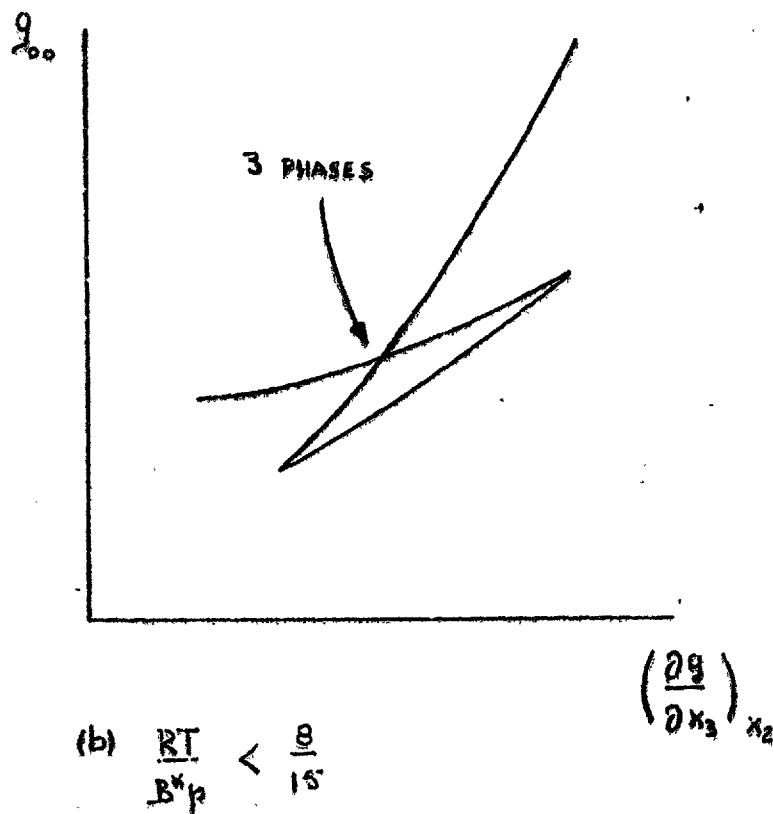
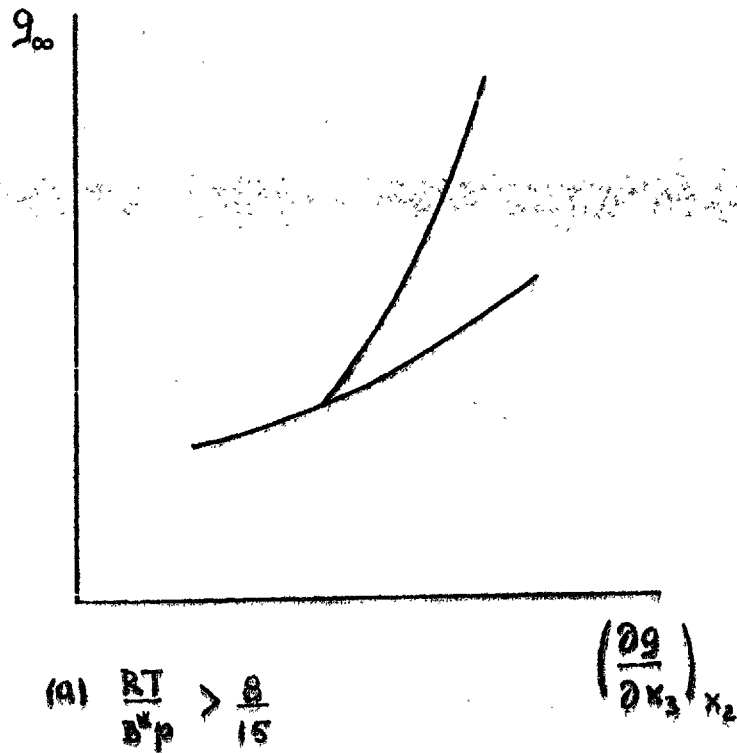


Figure 26 Procedure to compute the vertices of the three-phase triangle from the Gibbs free energy.

computing

$\left(\frac{\partial g_m}{\partial x_3}\right)_{x_2}$ and $g_{oo} = g(x_2, x_3) - \left(\frac{\partial g_m}{\partial x_3}\right)_{x_2}$ along the binodal and then plotting $\left(\frac{\partial g_m}{\partial x_3}\right)_{x_2}$ against g_{oo} (Figure 26).

The intersection leads to the coordinates of these points as outlined in section III.5.

At $RT/B^*p = 0.432218$ ($\pi = 4.627289$) the three apices meet at the centre and the six lower corners merge in pairs at the lines of symmetry; four-phase equilibrium is then established. Below this the temperature there is a single three-phase region which fills most of the coordinate triangle, covering eventually the entire triangle at $RT/B^*p = 0$ ($\pi = \infty$).

The secondary branches which the binodal develops below the tri-critical temperature can be determined by a procedure similar to the one used to obtain the vertices of the three-phase triangles, but enquiring about $\left(\frac{\partial g_m}{\partial x_3}\right)_{x_2}$ and g_{oo} along the locus where $\left(\frac{\partial g_m}{\partial x_2}\right)_{x_3}$ is a non-zero constant instead of being zero; this locus is found by solving iteratively (3-101) with the non-zero gradient $\left(\frac{\partial g_m}{\partial x_2}\right)_{x_3}$ included; $L(x_2, x_3)$ of (3-101) becomes then

$$L(x_2, x_3) = \frac{1 - 2x_2 - x_3}{c + \log \left[\frac{1 - x_2 - x_3}{x_2} \right]} + \frac{1 - 2x_2 - x_3}{x_2 + x_3 - x_2^2 - x_2 x_3} \quad (3-105)$$

with

$$c = \frac{1}{RT} \left[\frac{\partial g}{\partial x_2} \right]_{x_3} = \text{constant} \quad (3-106)$$

The secondary branches are cumbersome to evaluate because of the lack of symmetry, but as they add no further physical understanding of the phase behaviour we consider them no more.

III.12 Discussion

The MFA gives complete information on the phase separation of the ternary mixture, which conforms to the "normal" tricritical point pattern. Both the bicritical and the tricritical points are classical, the former because only two phases are involved and consequently all conclusions from chapter II apply, and the latter because the tricritical exponents assume their "classical" value, i.e. those of Griffiths's model [33]. In the next chapter the phase diagram of the mixture is studied with a three- to six-term virial expansion and the tricritical behaviour analyzed. From this analysis it is concluded that the MFA description of the tricritical singularities is quantitatively correct to this number of coefficients and probably for any number of them.

Chapter IV

THE VIRIAL EXPANSION IN THE TERNARY MIXTURE MODEL

The MFA provides a qualitatively complete picture of the ternary mixture model but is exact only for a system of infinite dimensionality. We examine therefore in this chapter the phase behaviour of the model when the free energy is not restricted to the second virial coefficient. We find that the geometry of the phase diagram is unchanged, the tri-critical points are of the "normal" class since the three vanishing phases do so "asymmetrically", i.e. no three-fold symmetry is involved, and a quadruple point appears again at some higher pressure. Even more important is that the MFA description of the singularities at the tri-critical point is correct no matter how many virial coefficients are included (up to six which are available), thus strongly suggesting that Griffiths's conjecture of the correctness of the MFA prediction of tri-critical phenomena [33] is satisfied in this model.

The exact series, i.e. that where all integrals are considered, is studied; since only particles of different species have non-zero interactions it is possible to include higher order virial coefficients than in a more general model (with all interactions different from zero).

We begin by considering the virial expansion of the free energy density given by

$$a = a_0 - \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \rho_a^i \rho_b^j \rho_c^k c_{ijk} \quad (4-1)$$

where c_{ijk} is the contribution of the term $\rho_a^i \rho_b^j \rho_c^k$ to the $(i+j+k)$ th virial coefficient. For simplicity of notation we define

$$c_{000} = c_{100} = c_{010} = c_{001} = 0 \quad (4-2)$$

For the intermolecular potentials of the mixture model the Mayer functions f_{aa} , f_{bb} and f_{cc} are zero, therefore all coefficients c_{iii} vanish.

The numerical value of c_{ijk} is obtained from the theory of virial expansion [87, 88, 89] as the sum of all integrals of products of Mayer functions involving $i+j+k$ particles; those are called cluster integrals.

A considerable mathematical manipulation is required to deal with the statistical derivation of the equation of state in virial form. The problem was first solved exactly by Ursell [87] and later greatly simplified by Mayer [88] and has since been discussed by many other authors and applied to thermodynamic and statistical quantities [89].

The cluster integrals are most simply discussed in terms of the theory of graphs from which we introduce some definitions [55].

IV.1 Some definitions of graph notation

i) A linear graph, denoted by G_{pq} , is a collection of p points and q lines connecting certain pairs of those points. The p points represent the molecules involved in the cluster integral from which G_{pq} forms part; the lines usually represent the Mayer function $f(r)$, although sometimes it is convenient to represent other functions like $rf(r)$ or $c(r)$. In the following we consider only $f(r)$ bonds.

ii) The graph is disconnected if it is possible to separate the points in two or more groups such that there is no line joining the distinct groups. It is connected if the separation is not possible.

iii) A graph is said to be coloured if different species are assigned to the points. In all that follows we will deal with tri-coloured graphs.

iv) If one point is given a special designation that point is called a root point, if not it is called a field point. A root becomes a field point upon integration over its coordinates. Graphs with root points are rooted graphs; graphs with no roots are free graphs.

v) If all points are distinguishable we have a labelled graph, otherwise the graph is unlabelled. Roots are always distinguishable.

vi) A connected graph is irreducible if there is no point such that on cutting all lines attached to it the graph becomes disconnected, otherwise the graph is reducible. If the cutting point is such that one of the pieces is free from roots it is called an articulation point.

vii) In the theory of virial expansions only connected graphs without articulation points are considered; those graphs are called stars. A polygon is the simplest star, for it involves the minimum number of lines for a given set of points. On the other extremum we have a complete star where every point is joined to the rest.

IV.2 The value of the graphs. The gaussian model

In virial expansions all possible stars involving two, three, etc. points are considered. The number of graphs as well as the difficulty

of computing their value increases very rapidly. In the model used here the simplification introduced by the fact that f_{aa} , f_{bb} and f_{cc} vanish reduces considerably the number of stars involved.

In computing the virial coefficients we must face two separate problems, one is the actual computing of the value of the stars, the other is to count the total number of stars contributing to each coefficient. This last involves formidable combinatorial problems, many of them still unsolved.

The value of the graph can be obtained in closed form for the gaussian model discussed previously in Chapters I and II. In this model the Mayer function assumes the form

$$f_{ij}(r) = -\exp(-\alpha^2 |\underline{r}_i - \underline{r}_j|^2) \quad (4-3)$$

$$= -\exp(-\alpha^2 r^2) \quad (4-4)$$

The graph G_{pq} represents the integral $W(G_{pq})$,

$$W(G_{pq}) = \frac{1}{V} \int \dots \int \prod_{\{G_{pq}\}} f_{ij} d(p) \quad (4-5)$$

where the product is over all bonds of G_{pq} . Introducing (4-3) yields

$$W(G_{pq}) = \frac{(-1)^k}{V} \int \dots \int \exp\{-\alpha^2 \sum_{\{q\}} |\underline{r}_i - \underline{r}_j|^2\} d(p) \quad (4-6)$$

where the sum is over all q bonds of G_{pq} . This sum can be written as a simple quadratic form with the introduction of a matrix containing the structure of the graph. Let $||D(G_{pq})||$ be $p \times p$ matrix associated with G_{pq} whose elements are defined by

$$i) \text{ when } i \neq j \quad D_{ij}(G_{pq}) = \begin{cases} -1 & \text{if the link } i-j \text{ occurs in } G_{pq}. \\ 0 & \text{if the link does not occur.} \end{cases} \quad (4-7)$$

ii) when $i = j$ $D_{ii}(G_{pq}) =$ the number of bonds attached to the point i .

With this definition, the sum in the integrand of (4-6) becomes

$$\sum_{\{q\}} |\underline{r}_i - \underline{r}_j|^2 = \sum_{i=1}^p \sum_{j=1}^p D_{ij}(G_{pq}) \underline{r}_i \cdot \underline{r}_j \quad (4-8)$$

The quadratic form (4-8) as it stands cannot be further reduced because the determinant of $D(G_{pq})$ is zero, however any one of the coordinates r_i may be eliminated by a suitable redefinition of the origin. Let primed variables refer to the new origin, then

$$\sum_{i=1}^p \sum_{j=1}^p D_{ij}(G_{pq}) r_i \cdot r_j = \sum_{i=1}^{p-1} \sum_{j=1}^{p-1} D_{ij}(G_{pq}) r'_i \cdot r'_j \quad (4-9)$$

Let $d(G_{pq})$ be the determinant of the quadratic form on the right hand side of (4-9) obtained from $D(G_{pq})$ by striking out the first (or last) row and the first (or last) column; we call it the graph complexity.

Since $d(G_{pq})$ is not zero, a linear transformation can reduce the quadratic form to a normal form, i.e. to a form where its equation contains no term in r_i except the term r_i^2 [90]. After some algebra (see ref. [90b]) we have, in three dimensions,

$$W(G_{pq}) = (-1)^k \left(\frac{\pi}{\alpha} \right)^{\frac{3}{2}(p-1)} [d(G_{pq})]^{-\frac{3}{2}} \quad (4-10)$$

IV.3 The problem of counting stars

The problem of counting the stars is more difficult since there is no systematic way of solving it.

The coefficient c_{ijk} is the sum of all stars with i field points of species a and j and k of species b and c . Any labelling of the points as well as any permutation of species does not change the value of G_{pq} although it constitutes a different configuration and therefore must be counted in the sum.

Consequently we must take into account how many graphs identical in value can be generated by a mere labelling of points and interchange of species.

Let us write

$$v_o^{i+j+k-1} c_{ijk} = \sum_{\{G_{pq}\}}^S \frac{m}{s} W(G_{pq}) \quad (4-11)$$

where $\sum_{\{G\}}^S$ means the sum over all graphs with p points ($p = i+j+k$) and q lines. $W(G_{pq})$ is the value of G_{pq} given by eq (4-10).

m is called the mixture labelling factor and s the symmetry number of the graph; their ratio gives the total number of graphs identical in value.

Consider a free unlabelled graph G_{pq} and let for the moment all p points be of the same species. $p!$ permutations are possible among the points. Let n be the number of ways of labelling the graph all leading to equivalent results, i.e. involving the same (labelled) Mayer functions. The symmetry of the graph is the ratio

$$s = \frac{p!}{n} \quad (4-12)$$

Let now G_{pq} be a coloured graph. In addition to permutations of labels, permutation of species must also be considered, thus the graph



and the graph



are identical in value but represent different configurations amongst the species. m , the mixture labelling factor, is the number of graphs obtained from G_{pq} by interchange of species, as from (4-13) to (4-14).

For bicoloured graphs there are only two possibilities. When $i \neq j$ there is only one way of assigning the species to the points without establishing a bond between like species. When $i = j$ there are two ways [41]. The mixture labelling factor is thus

$$m = 1 + \delta_{ij} \quad (4-15)$$

where δ_{ij} is Kronecker's delta.

For tricoloured graphs there is no known rule, m then must be obtained by counting in how many different ways a monochromatic (one-component) graph may be coloured.

IV.4 Colouring trees

Tricoloured stars were obtained first by colouring each p -sided monochromatic polygon of the list of Hoover and DeRocco [91] in every possible way and then adding the bonds until a complete star was considered. Naturally all graphs involving any link between like species were discarded. To check that no coloured polygon was excluded a "colouring" tree was used.

We start with a "base point" being of any species, c for example. Two bonds are possible, $c-a$ and $c-b$, the end points, a and b can have each two bonds, $a-b$ and $a-c$ for a and $b-a$ and $b-c$ for b . Adding each time the only two choices the process is carried out until p points are considered along every "branch". A five-point tree is shown in Figure 27.

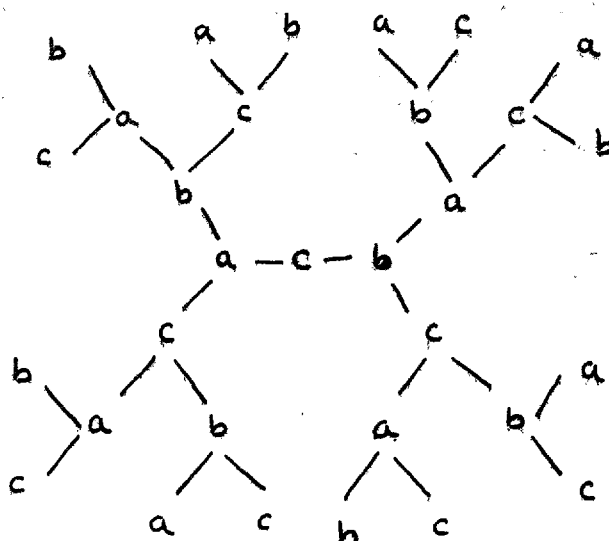


Figure 27. The five-point colouring tree with base point of species c .

All branches on which the final point is of the same species as the base are discarded since on closing the path a zero bond is established. The rest of the paths yield all polychromatic polygons.

In this way all colourings are considered for odd-sided polygons and all but one for even-sided polygons; the missing configuration in the second case is just the polygon with $p/2$ points of species a and $p/2$ of species b distributed alternately.

The mixture labelling factor is deduced when the number of identical graphs is counted. Extreme care was taken in considering all graphs but no independent check was found; nevertheless the results should be reliable.

The stars contributing to the exact c_{ijk} up to the sixth virial coefficient are listed in Table VII. The coefficient of each graph is the ratio m/s . In Table VIII the values of the coefficients c_{ijk} are listed.

IV.5 Three-component virial expansions

So far we have considered the virial series only up to the second virial coefficient. With the aid of the gaussian model we are now in a position to include higher order coefficients.

Consider the virial expansion of the free energy,

$$\frac{A}{kT} = \frac{A_0}{kT} - \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{N_a^i N_b^j N_c^k}{v^{i+j+k-1}} c_{ijk} \quad (4-16)$$

where c_{ijk} is the molecular $(i+j+k)$ th virial coefficient. Consistently with (4-2) we define $c_{000} = c_{100} = 0$.

The pressure and chemical potential are derived in the usual way giving

$$\frac{p}{kT} = \frac{(N_a + N_b + N_c)}{v} - \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} (i+j+k-1) \frac{N_a^i N_b^j N_c^k}{v^{i+j+k}} c_{ijk} \quad (4-17)$$

and

$$\frac{\mu_a - \mu_a^*}{kT} = \log \left(\frac{N_a kT}{p v} \right) - \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} i \frac{N_a^{i-1} N_b^j N_c^k}{v^{i+j+k-1}} c_{ijk} \quad (4-18)$$

In terms of the reduced variables the last two equations read

$$\pi = \rho_a + \rho_b + \rho_c - \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} (i+j+k-1) \rho_a^i \rho_b^j \rho_c^k c_{ijk} \quad (4-19)$$

and

$$\log z_a = \log \rho_a - \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} i \rho_a^{i-1} \rho_b^j \rho_c^k c_{ijk} \quad (4-20)$$

$$C_{110} = \text{---} \circ \text{---} \times$$

$$C_{111} = \frac{1}{6} \begin{array}{c} \times \\ \diagup \quad \diagdown \\ \circ \text{---} \times \end{array}$$

$$C_{220} = \frac{1}{4} \begin{array}{c} \times \quad \circ \\ \text{---} \quad \text{---} \\ \circ \quad \times \end{array}$$

$$C_{221} = \frac{1}{4} \begin{array}{c} \times \quad \circ \\ \text{---} \quad \text{---} \\ \circ \quad \times \end{array} + \frac{1}{2} \begin{array}{c} \times \quad \circ \\ \diagdown \quad \diagup \\ \circ \quad \times \end{array}$$

$$C_{230} = \frac{1}{12} \begin{array}{c} \circ \\ \diagup \quad \diagdown \\ \times \quad \times \\ \diagdown \quad \diagup \\ \circ \quad \times \end{array}$$

$$C_{122} = \frac{1}{10} \begin{array}{c} \times \quad \times \\ \diagdown \quad \diagup \\ \circ \quad \times \end{array} + \frac{1}{10} \begin{array}{c} \times \quad \times \\ \diagdown \quad \diagup \\ \circ \quad \times \end{array} + \frac{1}{2} \begin{array}{c} \times \quad \times \\ \diagdown \quad \diagup \\ \circ \quad \times \end{array} + \frac{1}{2} \begin{array}{c} \times \quad \times \\ \diagdown \quad \diagup \\ \circ \quad \times \end{array} + \frac{1}{8} \begin{array}{c} \times \quad \times \\ \diagdown \quad \diagup \\ \circ \quad \times \end{array} + \frac{1}{6} \begin{array}{c} \times \quad \times \\ \diagdown \quad \diagup \\ \circ \quad \times \end{array}$$

$$C_{330} = \frac{1}{6} \text{ (hexagon)} + \frac{1}{2} \text{ (hexagon with vertical line)} + \frac{1}{4} \text{ (hexagon with two diagonals)} + \frac{1}{36} \text{ (hexagon with three diagonals)}$$

$C_{123} = \frac{1}{12}$
 $+$
 $\frac{1}{2}$
 $+$
 $\frac{1}{2}$
 $+$
 2

$+\frac{1}{2}$

 $+\frac{1}{4}$

 $+\frac{1}{6}$

 $+\frac{1}{2}$


$+\frac{1}{2}$

 $+\frac{1}{12}$

 $+\frac{1}{36}$

 $+\frac{1}{4}$


$$\begin{aligned}
 C_{222} = & \frac{1}{12} \text{ (hexagon with X at top and bottom vertices, O at other four)} + \frac{3}{2} \text{ (hexagon with X at top and bottom vertices, O at other four, with horizontal internal lines)} + \frac{3}{2} \text{ (hexagon with X at top and bottom vertices, O at other four, with vertical internal lines)} + \frac{3}{4} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines)} \\
 & + \frac{3}{4} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square)} + \frac{1}{6} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line)} + 3 \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line)} + \frac{3}{2} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line)} \\
 & + \frac{1}{2} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line, and one more diagonal line)} + \frac{3}{16} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line)} + \frac{3}{16} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line)} + \frac{1}{4} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line)} \\
 & + \frac{1}{48} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line)} + \frac{3}{16} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line)} + \frac{3}{16} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line)} + \frac{3}{16} \text{ (hexagon with X at top and bottom vertices, O at other four, with both horizontal and vertical internal lines, and two diagonal lines forming a square, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line, and one more diagonal line)} \\
 C_{240} = & \frac{1}{48} \text{ (pentagon with X at top and bottom vertices, O at other three)} \\
 C_{114} = & \frac{1}{48} \text{ (pentagon with X at top and bottom vertices, O at other three, with one internal line)} + \frac{1}{48} \text{ (pentagon with X at top and bottom vertices, O at other three, with one internal line, and one more internal line)}
 \end{aligned}$$

Table VII Cluster integrals contributing up to the sixth virial coefficient in the ternary mixture model.

Second virial coefficient	$c_{110} = - 1.0000000$
Third virial coefficient	$c_{111} = - 0.0589256$
Fourth virial coefficient	$c_{220} = 0.0312500$
	$c_{211} = 0.0091529$
Fifth virial coefficient	$c_{230} = 0.0020047$
	$c_{122} = - 0.0248322$
Sixth virial coefficient	$c_{330} = 0.0038529$
	$c_{123} = 0.0015291$
	$c_{222} = - 0.0324958$
	$c_{240} = 0.0001151$
	$c_{114} = 0.0000524$

Table VIII. The first six virial coefficients.

where $c_{ijk} = v_o^{-(i+j+k-1)} \epsilon_{ijk}$.

IV.6 Two-phase region

Two-phase equilibria subsist as long as the symmetry conditions

$$\rho'_a = \rho''_b$$

$$\rho'_b = \rho''_a$$

(4-21)

$$\rho'_c = \rho''_c$$

are satisfied, that is, for $\pi < \pi_{TC}$. Below the tricritical pressure the phase boundary is given simply by

$$\log(\rho_a/\rho_b) = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=0}^{\infty} (i \rho_a^{i-1} \rho_b^j - j \rho_a^i \rho_b^{j-1}) \rho_c^k c_{ijk} \quad (4-22)$$

Any particular tie-line is obtained by solving (4-19) and (4-22) at fixed π and constant ρ_c . The two equations are easily solved with a Newton-Raphson method [85] since their derivatives are expressed simply in closed form.

IV.7 Stability and critical lines

The locus of bicritical points is determined by the intersection of the lines $D = 0$ and $D' = 0$. This case is more complicated than the MFA, for the elements of the two determinants are polynomials of the $(i+j+k-2)$ th degree in $\rho_a \rho_b \rho_c$. Their form becomes too cumbersome to permit a closed solution; nevertheless the expansion in cofactors (which are evaluated independently) though lengthy is straightforward. The resulting equations are solved by a three dimension Newton-Raphson method.

Tricritical points correspond to bifurcation of the critical lines, that is, the points where the equation $D = 0$ and $D' = 0$ change from having only one solution to having three. One disadvantage of Newton-Raphson method is that it searches only for the solution closest to the initial guess supplied; this causes some difficulty in finding all three solutions, for $\pi \gtrsim \pi_{TC}$, particularly near the tricritical point where the three solutions are very close to each other. Although this fact imposes some limitation on the accuracy in locating the tricritical point, it does not invalidate the method for examining the angle of bifurcation of the

critical lines.

The procedure was carried out several times, each time including one more virial coefficient.

The case with two coefficients is the mean field result. Inclusion of the third changes the phase diagram very little, however from the fourth onwards some difficulty was experienced in obtaining three solutions at each pressure above and near the critical. Nevertheless in all cases the critical line bifurcates at right angles to the line of symmetry to within the computational uncertainty. The estimated critical exponents from the log-log plots (Table X) θ_1 and θ_{II} are all within the range $\theta_1 = 0.5 \pm 0.05$ and $\theta_{II} = 2.0 \pm 0.2$. A better estimate of the tricritical pressure is obtained from the development of the three-phase triangles into which the tricritical point splits.

IV.8 Tricritical point

Following the procedure described in section III.5 we obtain the vertices of the three-phase triangles for any pressure between the tricritical and quadruple points. The value of the tricritical pressure and the shape of the three-phase triangles were investigated with the successive inclusion of the virial coefficients. The second virial coefficient gives the MFA and the third changes the diagram little. Larger changes were observed with the inclusion of the fourth and higher order coefficients. It soon became apparent that the series was being truncated too early, since the tricritical pressure, and tricritical density of one of the components, increased steadily with the number of coefficients considered (see Table IX and Figure 28). It is possible that several more coefficients are necessary in order to achieve stable behaviour. Such was the experience of other workers in their study of the binary mixture [40, 43].

In spite of the unsettled behaviour, and in contrast with it, the characteristic "flatness" of the three-phase triangles in the tricritical neighbourhood remains unchanged. Very small variations are found in the values of the tricritical indices β_1 and β_2 (Table X) all lying close to their MFA values $\beta_1 = 0.5$ and $\beta_2 = 1.0$. The linear development of the three-phase triangles provides a simple and accurate way to obtain the value of π_{TC} .

More important is that the flatness of the three-phase triangles in the tricritical region indicates that the three coexisting phases into which the tricritical point splits do not form with three-fold symmetry, but rather a well-defined direction in the composition space, oblique to the line of symmetry, is singled out. This is consistent with the

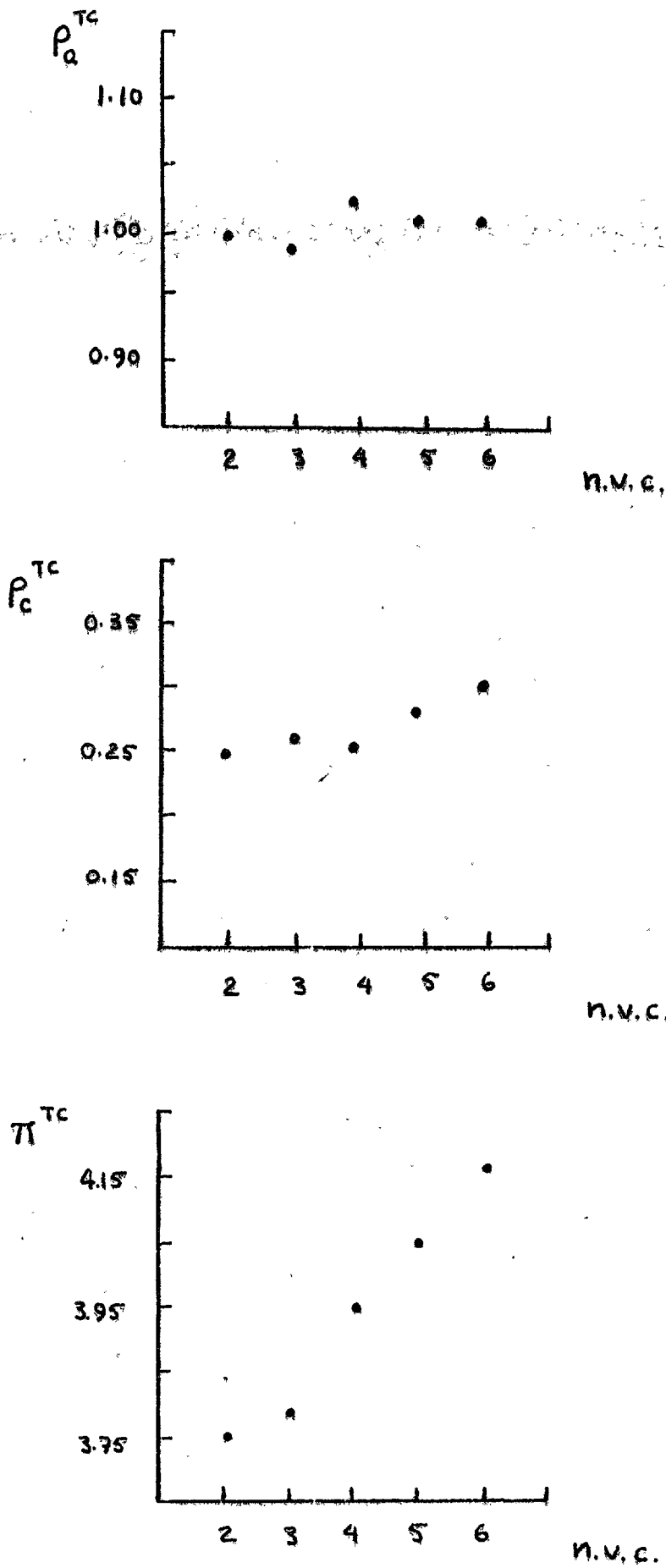


Figure 28 Displacement of the tricritical point with the number of virial coefficients (n.v.c) .

Number of coefficients	π	$p_a = p_b$	p_c
2 (MFA)	3.75	1	0.25
3	3.764 $\pm$ 0.002	0.9899	0.2686
4	3.946 $\pm$ 0.002	1.0593	0.2637
5	4.047 $\pm$ 0.002	1.0354	0.3185
6	4.160 $\pm$ 0.002	1.0328	0.3624

Table IX Successive approximations to the tricritical point. The error bars represent the interval of confidence of results.

n.v.c.	2	3	4	5	6
β_1	$\frac{1}{2}$	0.50	0.48	0.51	0.50
β_2	1	1.0	1.0	1.0	1.0
θ_{11}	2	1.8?	2.2	2.0	2.1
θ_1	$\frac{1}{2}$	0.45?	0.55	0.5	0.5

Table X Tricritical exponents β_1 , β_2 , θ_{11} and θ_1 as function of the number of virial coefficients (n.v.c.)

Number of coefficients	<i>lower corner</i>		<i>centre</i>	π
	p_a	$p_b = p_c$	p	
2 (MFA)	3.6138	0.1086	0.8388	4.627
3	3.4176	0.1238	0.8189	4.533
4	3.6076	0.1196	0.8619	4.689
5	3.2948	0.1553	0.8361	4.599
6	3.1515	0.1774	0.8317	4.581

Table XI Successive approximations to the quadruple point.

single-order-parameter theory of Griffiths [33] and thus with a "normal" phase diagram of the kind of the MFA, and rules out any "anomalous" tricritical point of the kind obtained by Straley and Fisher [32]. The occurrence of normal tricritical points is underlined by the geometry of the phase diagram which leads to an equilibrium quadruple point which is discussed next.

IV.9 Quadruple point

At sufficiently high pressure the three-phase regions join, forming a point of four-phase equilibrium. Computation of the activities at the centre and lower corners of each triangle shows that the point is indeed stable. A simple set of equations of which those of the MFA are a particular case (Equations (3-78), (3-81) and (3-82)) are sufficient to locate the point.

As for the tricritical point, determination of the quadruple point shows that the series is also incomplete, giving particularly poor estimates of the densities of the three components at the lower corners. The pressure, though, is well defined and does not deviate much from its MFA value. The results are shown in Table XI and Figure 29.

Further increase of the pressure makes the quadruple point disappear and a single three-phase region forms in the middle of the coordinate triangle. The transition is of first order, i.e. no macroscopic fluctuations are involved in any thermodynamic variable. Our truncated series thus indicate that the MFA behaviour persists even when higher coefficients are included.

IV.10 Discussion

It is clear from the results above that the geometry of the phase diagram is the same in the truncated virial expansions of this chapter as in the MFA. The model displays three-phase equilibria, beginning at three normal tricritical points and ending in a quadruple point at higher pressures. Such is the behaviour of Meijering's regular solutions [50] and of the quaternary mixture studied experimentally by Lang and Widom [70]. More specifically it is found that the MFA values of the tricritical indices remain unchanged up to a six-term virial series and presumably also in the exact case. This is a feature of higher-order critical points and there is still much work to be done in order to clarify why tricritical points are of such different nature to ordinary (bi) critical points.

The model discussed in this and the previous chapter has the three-fold symmetry of the three-state Potts model. In fact we regard it as a

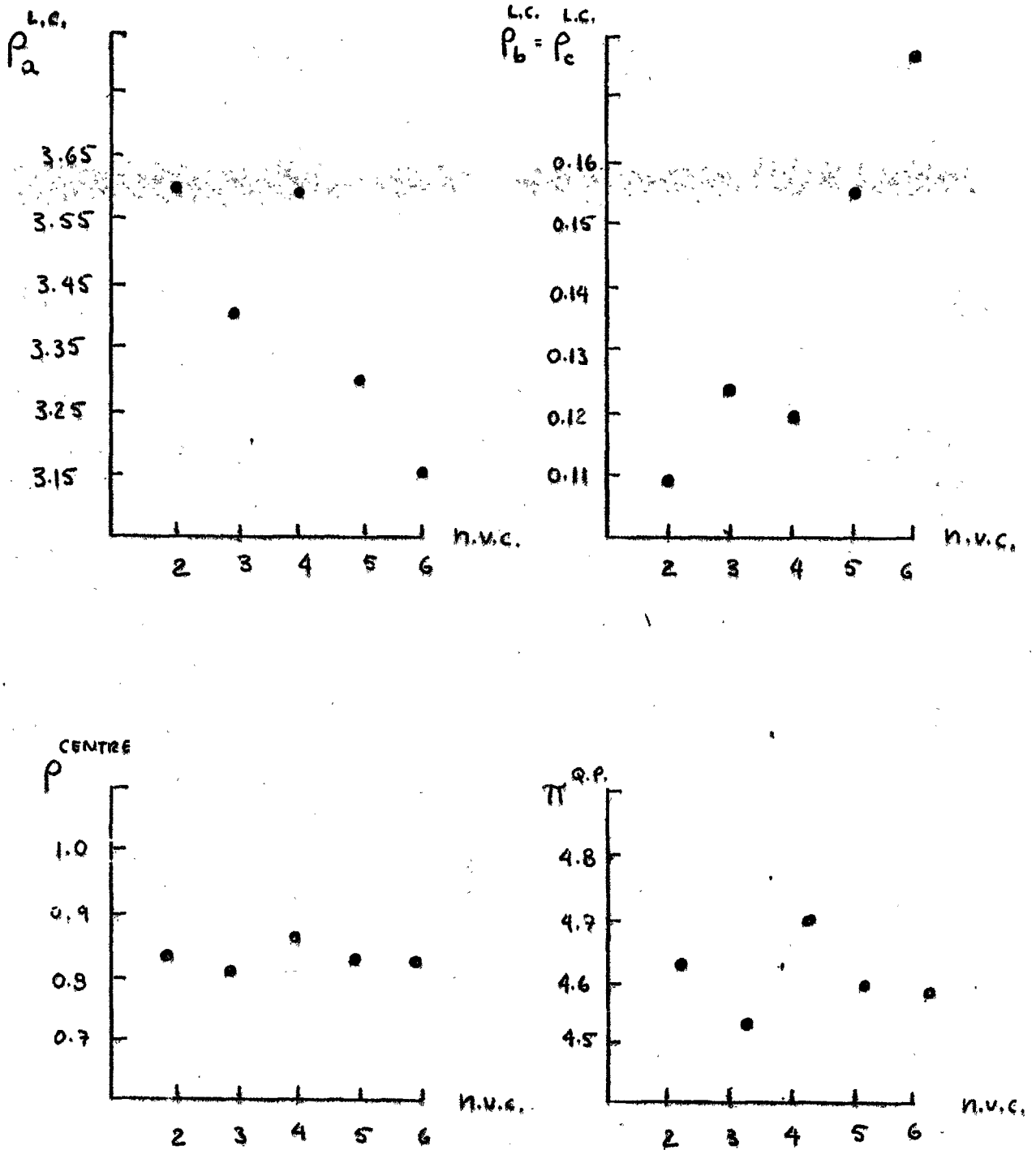


Figure 29 Displacement of the quadruple point with the number of virial coefficients (n.v.c.) .

generalization of that model to a continuum system in the same way that the original penetrable-sphere model was proposed as a generalization of the lattice gas. It is not clear, then, why the phase diagrams of the three-component continuum system and the three-state Potts model are different. The continuum nature of the former against the discrete nature of the latter might be one reason. These are not the only two models leading to contradictory phase diagrams, there is a whole class of models which may be put into two groups, in the one the Potts model (the anomalous-tricritical-point models) and in the other this continuum model (the normal-tricritical-point models). These were briefly reviewed in the introduction to Chapter III. For the second group there is experimental evidence, though in an asymmetric system.

It would be of much interest to extend the present model to an asymmetric ternary mixture ($u_{ab} \neq u_{bc} \neq u_{ca} \neq u_{ab}$) and to a quaternary mixture, which would be closer to experiment. Also an experiment, whether simulated on a computer or in the laboratory, on a three-fold symmetric system may well prove whether the above description of the phase diagram is true or not.

The nature of the bicritical point has been discussed at length in the past (see particularly Fisher [12]); in the next chapter we consider that question first in the context of the penetrable-sphere model and then in a Lennard-Jones fluid.

Chapter V

THE PERCUS-YEVICK AND HYPER-NETTED CHAIN APPROXIMATIONS IN THE NEIGHBOURHOOD OF THE CRITICAL POINT

In the past chapters bicritical and tricritical points have been discussed in the two-component version of the penetrable-sphere model and its extension to a ternary mixture model.

For bicritical points there is conclusive evidence for non-classical behaviour [12], therefore mean-field theories are useful but essentially incorrect near the bicritical point. Tricritical points, on the contrary, are of classical nature, at least for systems which follow the "normal" pattern, like the one studied in Chapters III and IV.

The penetrable-sphere model, in spite of its artificial potential, behaves in closer agreement with real fluids than a mean field theory. The critical point in the two-component exact virial series for the hard-sphere and gaussian interactions is non-classical [40, 41]. The tricritical point in the ternary mixture follows the pattern of a normal tricritical point, which is supported by experimental evidence [70].

In this chapter we return to one- and two-component models to study the nature of the bicritical point with the help of the integral equation approximations.

Of all the equations proposed those of Percus and Yevick (PY) and the hyper-netted chain (HNC) [45] are the simplest which give physically reasonable results. They have been applied successfully over the whole thermodynamic space [17, 92, 93] and more recently in the critical region [40-42, 94-97]. We examine them in this region in the two-component version of the penetrable-sphere model when molecules interact with gaussian potentials and in a one-component fluid where molecules interact with Lennard-Jones (12,6) potentials.

In the penetrable-sphere model with gaussian interactions, virial expansions up to the eleventh coefficient have been developed by Sawford [41]. Several Padé approximants [98] have been fitted to the truncated series in order to obtain an extrapolation to their critical behaviour. The critical exponents in the PY approximation correspond to those of a classical theory while those of the HNC are non-classical.

For the Lennard-Jones fluid the integral equations have been solved numerically for temperatures and densities near the critical, and critical exponents have been deduced from the divergence of thermodynamic quantities.

Some previous work has been carried out. Melnyk, Rowlinson and Sawford [40] and Sawford [41] studied the virial expansion in powers of

the density of the hard-spheres and gaussian models and concluded that the PY approximation is classical. Later Ahn and Lebowitz [46] solved analytically this approximation for the hard-spheres model and confirmed its classical nature. For the Lennard-Jones fluid, Watts studied the PY [94] and the HNC [95] integral equations using Baxter's modification of the Ornstein-Zernike equation [99] which is less susceptible to errors arising from the truncation of the range of the correlation functions but is only exact for the PY. He found that there is a region of densities, below T_c , where neither equation has a solution. However, the isothermal compressibility is infinite only for the PY compressibility equation of state (equation (5-49) below). Henderson and Murphy [96] solved the PY integral equation using Baxter's modification and also using an iterative method based on the original PY equation [100], and concluded that both yield equivalent results provided that sufficiently large range of the integrations is used in the latter. They then used the former to compute the critical exponents and concluded that the PY predicts a classical critical point.

A) THE PENETRABLE-SPHERE MODEL

V.1 The PY and HNC approximations

Virial expansions may be carried out in the penetrable-sphere model to higher order terms because of the relatively small number of cluster integrals involved (all clusters with any link between like particles are zero).

A useful procedure to generate the graphs occurring in the virial expansion is to iterate over the integral equations substituting into themselves the result from one lower order iteration. In this section the PY and HNC are briefly discussed and the iterative procedure exemplified for the two-component PY equation. The integral equations are most conveniently expressed in terms of the function

$$y(r) = (1 + h(r)) (1 + f(r))^{-1} \quad (5-1)$$

where $h(r)$ and $c(r)$ are the total and direct correlation functions and $f(r)$ is the Mayer function.

The integral equations are most simply introduced by means of the theory of graphs. The correlation functions are defined as sets of rooted graphs (see section IV.1) and the integral equation approximations are prescriptions for those sets which, together with the Ornstein-Zernike (OZ) equation, define completely the correlation functions.

We introduce four classes of graphs,

- 1) The Mayer f function, denoted in what follows by $f = \text{O} \text{---} \text{O}$
- 2) The chains, which are those graphs with a "bridge point", i.e. one by which all routes from root 1 to root 2 must pass, and therefore without an f_{12} link. They will be denoted by $\mathbb{C} = \text{O} \text{---} \text{O} \text{---} \text{O}$
- 3) Bundles, in which are parallel routes from 1 to 2, one of which may be an f-bond. They will be denoted by $\mathbb{B} = \text{O} \text{---} \text{O} \text{---} \text{O}$
- 4) Elementary graphs, which are neither chains nor bundles. They are the most difficult to compute but are usually neglected. They will be denoted by $\mathbb{E} = \text{O} \text{---} \text{O} \text{---} \text{O}$

The correlation functions are defined in terms of these classes as follows [17]

$$h(r) = \text{all connected graphs without articulation points} \quad (5-2)$$

$$= f + \mathbb{C} + \mathbb{B} + \mathbb{E} \quad (5-3)$$

$$= f + (1 + f) \text{ (all connected graphs without f-bonds)} \quad (5-4)$$

$$= f + (1 + f) (\mathbb{C} + \mathbb{E}) \quad (5-5)$$

From (5-1) and (5-4)

$$y - 1 = \mathbb{C} + \mathbb{E} \quad (5-6)$$

From the proposition [17]

$$h - c = \mathbb{C} \quad (5-7)$$

and (5-3)

$$c = f + \mathbb{B} + \mathbb{E} \quad (5-8)$$

The PY and HNC approximations are obtained when some classes of graphs are neglected. Consider the expansion

$$\exp (\mathbb{C} + \mathbb{E}) - 1 = \mathbb{C} + \mathbb{E} + \{\mathbb{CE}\} \quad (5-9)$$

where

$$\{\mathbb{CE}\} = \sum_{j=2} \frac{(\mathbb{CE})^j}{j!}$$

is the set of all possible bundles of chains and elementary graphs. Equation (5-9) represents the set of all connected graphs without f-bonds, that is $y - 1$, therefore

$$y = \exp (C + D) \quad (5-10)$$

Defining

$$D = E + CE \quad (5-11)$$

we have

$$y = 1 + C + D \quad (5-12)$$

$$= 1 + h = C + D \quad (5-13)$$

but $h = (1 + f)y - 1$, therefore

$$c = f y + D \quad (5-14)$$

The direct correlation function comprises two terms, the first, fy , is of short range because of f ; the other, D , is a long-ranged but weak tail [101]. Since the essence of the PY approximation is to retain only the short-ranged term, the equations

$$\begin{aligned} c &= f y \\ D &= 0 \end{aligned} \quad (5-15)$$

defines the approximation; the correlation functions are: from (5-12), with $D = 0$,

$$y^{PY} = 1 + \text{diagram} \quad (5-16)$$

from (5-15)

$$c^{PY} = \text{diagram} + \text{diagram} \quad (5-17)$$

and from (5-5)

$$h^{PY} = \text{diagram} + \text{diagram} + \text{diagram} \quad (5-18)$$

The PY integral equation is obtained from (5-15) and the OZ equation

$$y^{PY} = 1 + n \int c^{PY}(r') h^{PY}(r-r') dr' \quad (5-19)$$

where n is the number density. Denote by $\otimes$ the convolution integral, then

$$y^{PY} = 1 + n c^{PY} \otimes h^{PY} \quad (5-20)$$

$$= 1 + n (f + f \otimes) \otimes (f + f \otimes + \otimes) \quad (5-21)$$

$$= 1 + n \left(\text{triangle} + \text{shaded triangle} + 2 \text{shaded triangle} + \text{shaded triangle} + \text{shaded triangle} \right) \quad (5-22)$$

It is clear from (5-22) what the prescription for the PY is: to form all polygons with non-crossing diagonals,

The HNC is less restrictive in the class of graphs neglected. From (5-10)

$$\log y = \otimes + \mathbb{E} \quad (5-23)$$

Setting $\mathbb{E}$, which is a subset of $\mathbb{D}$, equal to zero the HNC approximation is obtained

$$\log y^{HNC} = \otimes \quad (5-24)$$

$$= h^{HNC} - c^{HNC} \quad (5-25)$$

The correlation functions are

$$h^{HNC} = \text{triangle} + \text{shaded triangle} + \text{shaded triangle} \quad (5-26)$$

$$c^{HNC} = \text{triangle} + \text{shaded triangle} \quad (5-27)$$

$$y^{HNC} = \exp \left(\text{shaded triangle} \right) \quad (5-28)$$

and the HNC integral equation is

$$h - c = h \otimes c \quad (5-29)$$

but, by (5-25)

$$\log y = h \otimes c \quad (5-30)$$

Using (5-26) and (5-27) gives

$$\log y = (f + c + B) \otimes (f + B) \quad (5-31)$$

$$= \begin{array}{c} \text{---} \text{---} \\ \diagup \quad \diagdown \\ \circ \quad \circ \end{array} + 2 \begin{array}{c} \text{---} \text{---} \\ \diagup \quad \diagdown \\ \circ \quad \circ \end{array} + \begin{array}{c} \text{---} \text{---} \\ \diagup \quad \diagdown \\ \circ \quad \circ \end{array} + \begin{array}{c} \text{---} \text{---} \\ \diagup \quad \diagdown \\ \circ \quad \circ \end{array} + \begin{array}{c} \text{---} \text{---} \\ \diagup \quad \diagdown \\ \circ \quad \circ \end{array} \quad (5-32)$$

In the two-component integral equations all a-a, b-b and a-b correlations are considered. For the PY $f_{aa} = f_{bb} = 0$ means that also $c_{aa} = c_{bb} = 0$; for the HNC all correlations are non-zero. The iterative procedure to generate the graphs is illustrated here with the first few steps in the PY approximation.

For the binary mixture

$$c_{aa} = c_{bb} = 0 \quad (5-33)$$

$$c_{ab} = f_{ab} y_{ab} \quad (5-34)$$

$$y_{aa} = 1 + n_b c_{ab} \otimes h_{ab} \quad (5-35)$$

$$y_{ab} = 1 + n_a c_{ab} \otimes h_{aa} \quad (5-36)$$

$$h_{aa} = n_b c_{ab} \otimes h_{ab} \quad (5-37)$$

$$h_{ab} = y_{ab} - 1 + f_{ab} y_{ab} \quad (5-38)$$

and y_{bb} and h_{bb} are obtained from (5-35) and (5-37) by permuting species.

The iteration is started with the correlation functions in the limit of the infinitely diluted gas, where $h = c = f$ and $y = 1$, i.e.

$$c_{ab} = \text{---} \text{---} \quad (5-39)$$

$$h_{ab} = \text{---} \text{---} \quad (5-40)$$

The first order in density is

$$h_{bb} = n_a \begin{array}{c} \diagup \\ x \diagdown \end{array} \quad (5-41)$$

$$y_{aa} = 1 + n_b \begin{array}{c} \diagup \\ o \diagdown \end{array} \quad (5-42)$$

$$y_{ab} = 1 + n_a n_b \begin{array}{c} \diagup \\ o \diagdown \\ \diagup \\ o \diagdown \end{array} \quad (5-43)$$

where "o" and "x" denote root points of species a and b respectively and "o" and "*" are field points of species a and b. For the next order (5-41) to (5-43) are substituted into (5-34) to (5-38) to give

$$c_{ab} = o \text{---} x + n_a n_b \begin{array}{c} * \\ \diagup \diagdown \\ o \diagup \diagdown \\ x \end{array} \quad (5-44)$$

$$h_{ab} = o \text{---} x + n_a n_b \left(\begin{array}{c} * \\ \diagup \diagdown \\ o \diagup \diagdown \\ x \end{array} + \begin{array}{c} * \\ \diagup \diagdown \\ x \diagup \diagdown \\ o \end{array} \right) \quad (5-45)$$

which in turn produce

$$h_{bb} = n_a \begin{array}{c} \diagup \\ x \diagdown \end{array} + n_a^2 n_b \left(\begin{array}{c} * \\ \diagup \diagdown \\ x \diagup \diagdown \\ x \end{array} + 2 \begin{array}{c} * \\ \diagup \diagdown \\ x \diagup \diagdown \\ o \end{array} \right) \quad (5-46)$$

$$y_{aa} = 1 + n_b \begin{array}{c} \diagup \\ o \diagdown \end{array} + n_a^2 n_b^2 \left(\begin{array}{c} * \\ \diagup \diagdown \\ o \diagup \diagdown \\ o \end{array} + 2 \begin{array}{c} * \\ \diagup \diagdown \\ o \diagup \diagdown \\ x \end{array} \right) \quad (5-47)$$

$$y_{ab} = 1 + n_a n_b \begin{array}{c} \diagup \\ o \diagdown \\ \diagup \\ o \diagdown \end{array} + n_a^2 n_b^2 \left(\begin{array}{c} * \\ \diagup \diagdown \\ o \diagup \diagdown \\ x \end{array} + \begin{array}{c} * \\ \diagup \diagdown \\ x \diagup \diagdown \\ o \end{array} + 2 \begin{array}{c} * \\ \diagup \diagdown \\ o \diagup \diagdown \\ o \end{array} \right) \quad (5-48)$$

So the PY pattern (given in equation (5-22)) is developed. In principle the procedure can be carried out indefinitely, but the number of graphs increases very rapidly, soon making impracticable to obtain higher order terms.

V.2 The pressure and compressibility equations of state

There are two routes which will be followed to obtain the equation of state from the correlation functions, one, called the compressibility equation, results from the integration of the compressibility given by eq. (1-12), namely

$$\frac{1}{kT} \left(\frac{\partial p}{\partial n} \right)_T = 1 - n \int c(r) dr \quad (5-49)$$

The second is obtained by computing the ensemble average of the intermolecular virial function, $v(r) = r du(r)/dr$ [17] and is called the pressure equation of state,

$$\frac{p}{nkT} = 1 + \frac{1}{6} n \int r \frac{df(r)}{dr} y(r) dr \quad (5-50)$$

Equations (5-49) and (5-50) are entirely equivalent and consequently must lead to the same value of the pressure. However when the PY or HNC approximations are inserted, different values result. This inconsistency is due to the sets of graphs neglected.

The virial expansion of the pressure results from substituting the corresponding expansions of $c(r)$ and $y(r)$ into (5-49) and (5-50) and the critical behaviour follows by extrapolation towards the singularity with a Padé approximant, which is the ratio of two polynomials of degrees N and M (hence the notation (N,M)) whose coefficients are determined from the series which they replace. The critical value of the expansion variable is the closest-to-the-origin zero of the denominator and the critical exponent is the residue at that pole. Helfand and Stillinger [43] have discussed several applications of the method. Further details regarding the implementation for the penetrable-sphere model have been given by Sawford [41].

In the mixture model equations (5-49) to (5-50) must be transformed into two-component variables. The transcription between the one- and two-component models has already been discussed in detail in Chapter II. That transcription also insures that the critical exponents are the same in the two languages except from a "renormalization" between the two-component critical exponent γ_p and the one-component exponents γ and α . The renormalized index γ_p is given by [43]

$$\gamma_p = \frac{\gamma}{1-\alpha} \quad (5-51)$$

In the classical limit $\gamma_p = \gamma = 1$.

The nature of the critical point is most simply analysed by fitting a Padé to the function

$$\left[\frac{d \log(\partial^2 a / \partial x_a^2)}{d \rho} \right]_{\text{line of symmetry}} \quad (5-52)$$

where a is the two-component free energy density and $x_a = \rho_a / \rho$ is the mole fraction of particles of species a . The function (5-52) has a simple pole at $\rho_a = \rho_b = \rho_{\text{critical}}$ with residue γ_p [40]. The free energy density is obtained either from (5-49) or (5-50) by integration with respect to volume.

V.3 The PY approximation

The PY equation has been discussed in detail previously [40, 41] and here only the main results are quoted for comparison with the HNC.

The limiting behaviour of the series was obtained by forming Padé approximants of order (3,6), (4,5), (5,4), and (6,3). The results vary little and all yield a critical density within the range

$$\rho_a = \rho_b = 1.116 \pm 0.002 \quad (5-53)$$

and renormalized critical exponent

$$\gamma_\rho = 1.00 \pm 0.01 \quad (5-54)$$

This approximation has a smooth tendency to the asymptotic behaviour. Computation of the critical density from successive inclusion of virial coefficients leads to rapidly decreasing oscillations.

Since some lattice models have shown a sudden onset of classical behaviour as the dimensionality reaches 4 [102] the virial series was also studied for $d=4$ and $d=5$. The virial coefficients for 3, 4 and 5 dimensions are listed in Table XII. Naturally in this case there is no change, for the PY is already classical in three dimensions, but interesting changes are found in the HNC which is studied next.

V.4 The HNC approximation

Padé approximants of order (4,7), (5,6), (6,5) and (7,4) were formed both to the pressure and compressibility equations of state. In three dimensions the poles and residues are scattered, but the renormalized critical exponent is consistently greater than one.

Although no sudden onset of classical behaviour was observed for $d=4$, the scatter is appreciably smaller and the critical density and renormalized exponent are closer to their classical values. The absence of a sharp break at $d=4$ is probably due to an early truncation of the series and it is possible that the value of γ_ρ might fall to unity if more terms are considered. Such was the experience of Milosevic and Stanley [103] in their work on the spherical model.

The virial coefficients are listed in Table XIII and the critical density and renormalized critical exponents in 3, 4 and 5 dimensions are shown in Table XIV. The error bars correspond to the range spanned by the different approximants.

	D = 3	D = 4	D = 5
C(1,1)	-0.10000E 01	-0.10000E 01	-0.10000E 01
C(2,2)	0.20833E-01	0.10617E-01	0.52083E-02
C(3,3)	0.10434E-02	0.06296E-03	0.52651E-03
C(4,4)	0.10606E-04	0.15660E-03	0.10294E-03
C(5,5)	-0.15918E-04	0.34128E-04	0.28837E-04

TABLE XII VIRIAL COEFFICIENTS OF THE PY
APPROXIMATION FOR THE BINARY MIXTURE VERSION
OF THE PENETRABLE-SPHERE MODEL IN 3, 4 AND
5 DIMENSIONS.

D = 3

D = 4

D = 5

TABLE XIII VIAL COEFFICIENTS OF THE HNC
APPROXIMATION FOR THE BINARY MIXTURE VERSION
OF THE PENETRABLE-SPHERE MODEL IN 3, 4 AND
5 DIMENSIONS.

(P) REFERS TO THE PRESSURE EQUATION OF STATE
AND (C) TO THE COMPRESSIBILITY EQUATION.

	P	C	P	C	P	C
C(1,1)	-0.10000E-01	-0.10000E-01	-0.10000E-01	-0.10000E-01	-0.10000E-01	-0.10000E-01
C(2,2)	0.31250E-01	0.31250E-01	0.15625E-01	0.15625E-01	0.78125E-02	0.78125E-02
C(2,3)	0.20047E-02	0.20047E-02	0.57870E-03	0.57970E-03	0.16706E-03	0.16706E-03
C(2,4)	0.11509E-03	0.11509E-03	0.20345E-04	0.20345E-04	0.35965E-05	0.35965E-05
C(3,3)	0.27536E-02	0.46462E-02	0.24074E-02	0.29012E-02	0.13165E-02	0.14438E-02
C(2,5)	0.58231E-05	0.58231E-05	0.65104E-06	0.65104E-06	0.72789E-07	0.72789E-07
C(3,4)	0.10820E-02	0.10444E-02	0.36674E-03	0.32714E-03	0.10082E-03	0.87261E-04
C(2,6)	0.26703E-06	0.26103E-06	0.18838E-07	0.18838E-07	0.13595E-08	0.13595E-08
C(3,5)	0.22528E-03	0.17699E-03	0.37075E-04	0.28960E-04	0.55413E-05	0.43004E-05
C(4,4)	-0.65863E-03	0.54646E-03	0.38487E-03	0.73953E-03	0.32655E-03	0.41415E-03
C(2,7)	0.10462E-07	0.10462E-07	0.49429E-09	0.49429E-09	0.23355E-10	0.23355E-10
C(3,6)	0.35522E-04	0.24445E-04	0.30196E-05	0.22052E-05	0.25745E-06	0.18830E-06
C(4,5)	0.23165E-03	0.37249E-03	0.17871E-03	0.16691E-03	0.54405E-04	0.45654E-04
C(2,8)	0.37844E-09	0.37844E-09	0.11826E-10	0.11826E-10	0.36957E-12	0.36957E-12
C(3,7)	0.40850E-05	0.28623E-05	0.21155E-06	0.14892E-06	0.10641E-07	0.75189E-08
C(4,6)	0.17566E-03	0.13792E-03	0.36590E-04	0.26169E-04	0.53320E-05	0.36840E-05
C(5,5)	-0.46015E-03	-0.36396E-04	0.27020E-04	0.22194E-03	0.10034E-03	0.15140E-03
C(2,9)	0.12459E-10	0.12459E-10	0.25956E-12	0.25956E-12	0.54076E-14	0.54076E-14
C(3,8)	0.42622E-06	0.27734E-06	0.13175E-07	0.86578E-08	0.40115E-09	0.26566E-09
C(4,7)	0.54474E-04	0.35315E-04	0.52175E-05	0.32797E-05	0.40164E-06	0.24966E-06
C(5,6)	-0.92631E-04	0.82053E-04	0.74657E-04	0.83775E-04	0.29358E-04	0.25300E-04

	d = 3		d = 4		d = 5	
	ρ^c	γ_ρ	ρ^c	γ_ρ	ρ^c	γ_ρ
HNC(p)	1.19 ± 0.02	1.4 ± 0.1	1.073 ± 0.002	1.13 ± 0.01	1.0300 ± 0.0003	1.04 ± 0.01
HNC(c)	~ 1.25	~ 2	1.085 ± 0.003	1.19 ± 0.02	1.033 ± 0.001	1.05 ± 0.01

Table XIV. The critical density ρ^c and renormalized exponent γ_ρ for Padé approximants of the eleventh order in three, four and five dimensions.

B) THE LENNARD-JONES FLUID

The different nature of the critical point predicted by the PY and HNC approximations may be accounted by the fact that the latter alone has a direct correlation function with a weak but long-ranged tail which becomes crucial at the critical point. This is a feature of the approximation, not of the model, and therefore that difference should persist in a more realistic system. To show that this is the case in a Lennard-Jones fluid the PY and HNC integral equations have been solved numerically for temperatures and densities near the critical.

Consider a fluid whose molecules interact with the pair potential at a separation R

$$u(R) = \epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \quad (5-55)$$

where ϵ is an energy parameter and σ is the radius of the molecules. It is usual to introduce the reduced distance r , density ρ and temperature τ defined by

$$r = \frac{R}{\sigma}, \quad \rho = \frac{N\sigma^3}{V} \quad \text{and} \quad \tau = \frac{kT}{\epsilon} \quad (5-56)$$

In what follows we will work on that set of variables.

The critical point is located where the isothermal bulk modulus, $B_T(\rho, \tau)$, given by

$$B_T(\rho, \tau) = 1 - \rho \int c(r) dr \quad (5-57)$$

$$= (1 + \rho \int h(r) dr)^{-1} \quad (5-58)$$

first vanishes when the temperature is lowered from the one-phase region. Equation (5-57) is preferred to (5-58) because $h(r)$ is longer ranged than $c(r)$ and consequently more sensible to truncation errors.

V.5 The correlation functions

The correlation functions are given by the OZ equation and either (5-15) for the PY or (5-25) for the HNC. For computational purposes

it is more convenient to deal with the difference

$$\Delta(r) = h(r) - c(r) \quad (5-59)$$

rather than with either of the correlation functions,

From (5-15) and (5-59) the PY direct correlation function is given by

$$c^{PY}(r) = (1 + \Delta(r)) (\exp(-u(r) / \epsilon\tau) - 1) \quad (5-60)$$

and from (5-25) and (5-59) the HNC direct correlation function is

$$c^{HNC}(r) = \exp(\Delta(r) - u(r)/\epsilon\tau) - \Delta(r) - 1 \quad (5-61)$$

V.6 Numerical procedure

The integral equations are solved by the usual iterative procedure based on the fact that a Fourier transform of the OZ equations deconvolutes the integral [see ref.93, p.22 and references therein] ; thus

$$\tilde{h}(k) = \frac{\tilde{c}(k)}{1 - \rho \tilde{c}(k)} \quad (5-62)$$

where $\tilde{h}(k)$ and $\tilde{c}(k)$ are the (sine) Fourier transforms of $h(r)$ and $c(r)$

$$c(k) = \frac{4\pi}{k} \int_0^{\infty} r c(r) \sin(kr) dr \quad (5-63)$$

and similarly for $\tilde{h}(k)$. The inverse transform is given by

$$c(r) = \frac{1}{2\pi^2 r} \int_0^{\infty} k \tilde{c}(k) \sin(kr) dk \quad (5-64)$$

It is advantageous to use a modified form of (5-62), transforming

$\Delta(r)$ rather than $h(r)$ or $c(r)$ since $\tilde{\Delta}(k)$ has a shorter range than either of $\tilde{h}(k)$ or $\tilde{c}(k)$ thus allowing us to truncate the integration at shorter r [104].

The iterative procedure is defined as follows, a first estimate of $c(r)$ is transformed and substituted into

$$\Delta(k) = \frac{\rho[\tilde{c}(k)]^2}{\rho\tilde{c}(k)} \quad (5-65)$$

The function $\Delta(k)$ is then transformed back to configuration space; an improved estimate of $c(r)$ is obtained by either (5-60) for the PY or (5-61) for the HNC. The process is carried out until self-consistency i.e. no further improvement on $c(r)$ is observed. In practice iteration was stopped whenever

$$\max (|c_l(r_i) - c_{l-1}(r_i)|) < 10^{-4}, \quad i=1, \dots, N \quad (5-66)$$

where l refers to the l -th iterate and $c(r_i)$ is evaluated on the grid r_i , $i=1, \dots, N$.

For the first calculation the initial estimate was either the zero density limit for $r > 1$ and the PY hard sphere function [105] for $r < 1$,

$$c_0(r) = \begin{cases} \exp(-u(r)/\epsilon\tau) - 1 & r > 1 \\ a + b r^2 + c r^3 & r < 1 \end{cases} \quad (5-67)$$

where a , b and c are parameters depending only on density, or more usually a function from a nearby density and temperature.

The integrations involved in taking the Fourier transform were performed with a rule similar to the trapezoidal, with the intervals determined by the zeros of the sine functions. This procedure has recently been described by Lado [106]. The main advantage of this over equivalent methods, e.g. Filon's procedure [107], is that the orthogonality of the Fourier pair is preserved. This property reduces the numerical error when repetitive transforms are taken [108].

Lado's method assumes that both the functions and its transform vanish beyond a given range. Let L be such that $c(r)=0$ for $r \geq L$; the Fourier transform becomes then

$$c(r) \approx \frac{1}{2\pi r L} \sum_{j=0}^{\infty} k_j \tilde{c}(k_j) \sin(k_j r) \quad (5-68)$$

since $\sin(kL)=0$. The variable k_j is given by

$$k_j = \frac{j\pi}{L} = j\Delta k, \quad j = 0, 1, 2, \dots \quad (5-69)$$

and the integral of the inverse transform becomes of finite upper limit.

The further assumption that $\tilde{c}(k_j)$ vanishes for $k_j \geq N\pi/L$ leads to

$$c(r_i) = \frac{N^2}{2iL^3} \left[\frac{1}{N} \sum_{j=1}^{N-1} j \tilde{c}(k_j) \sin\left(\frac{ij\pi}{N}\right) \right] \quad (5-70)$$

and

$$\tilde{c}(k_j) = \frac{4L^3}{jN} \left[\frac{1}{N} \sum_{i=1}^{N-1} i c(r_i) \sin\left(\frac{ij\pi}{N}\right) \right] \quad (5-71)$$

where $r_i = iL/N = i\Delta r$ and the orthogonality condition states that

$$\Delta r \Delta k = \frac{\pi}{N} \quad (5-72)$$

The most important point for economizing computing time is to have an efficient algorithm to evaluate the trigonometric sums of (5-70) and (5-71). The fast Fourier transform of Cooley and Tukey [109] which is available in the Numerical Algorithm Group (NAG) library provided such algorithm [110].

The interval in configuration space, $\Delta r = L/N$, was taken to be

0.1 since a finer division did not improve significantly the values of the integrals. The longest distance considered was $L=12.8$, that is, a mesh of $N=128$ points. Near the critical point it is important to ensure that no significant contribution of the correlation functions is truncated. No appreciable change was detected for a longer range. The intermolecular potential was arbitrarily truncated at $r=6.4$. This distance is slightly larger than the usual cutoff radius ($r=6$) and probably accounts for the small differences in the critical density and temperature of this with respect to other works (see Table XV below), however, it should not affect the conclusions.

Both equations, but particularly the HNC, became unstable in the critical region. The initial estimate had to be very close to the solution to solve the equations along isotherms. Typical differences of $\Delta\rho = \frac{1}{10} \rho^c$ yielded a good estimate of neighbouring points outside the critical region, but here $\Delta\rho$ had to be as small as $\frac{1}{200} \rho^c$.

V.7 The critical point

At the critical point $B_T(\rho, \tau)$ vanishes for the first time on lowering the temperature from the one-phase region. For $\tau < \tau_c$, $B_T(\rho, \tau)$ has two zeros corresponding to the gas and liquid sides of the spinodal. Following the procedure described above the critical point was located and the shape of the critical isotherms investigated.

The PY and HNC equations behave quite differently as shown in Figures 30 and 31. The PY equation converges smoothly for all values of ρ and τ while the HNC becomes unstable near the critical point until it fails to converge. The difference is more explicit in Figure 32 where $B_T(\rho, \tau)$ is plotted as a function of temperature along the critical isochore. The PY equation yields a straight line consistently with the classical critical index $\gamma = 1$. The HNC on the contrary yields a line strongly curved near the critical temperature giving a value of γ much smaller than unity and probably even of zero. Thus the HNC is indeed singular but unphysical, since for real fluids $\gamma \sim 1.25$. An alternative but even less attractive possibility is that $B_T(\rho, \tau)$ is not zero at the "critical point" but the shape of Figure 31 does not suggest this.

In Table XV the values of ρ^c and τ are compared with previous results. The small differences for ρ^c in the PY approximation are attributed to the slightly longer range of the intermolecular potential in this work. The larger differences are in the HNC critical density and are probably due to the singularity found here. The error bars are

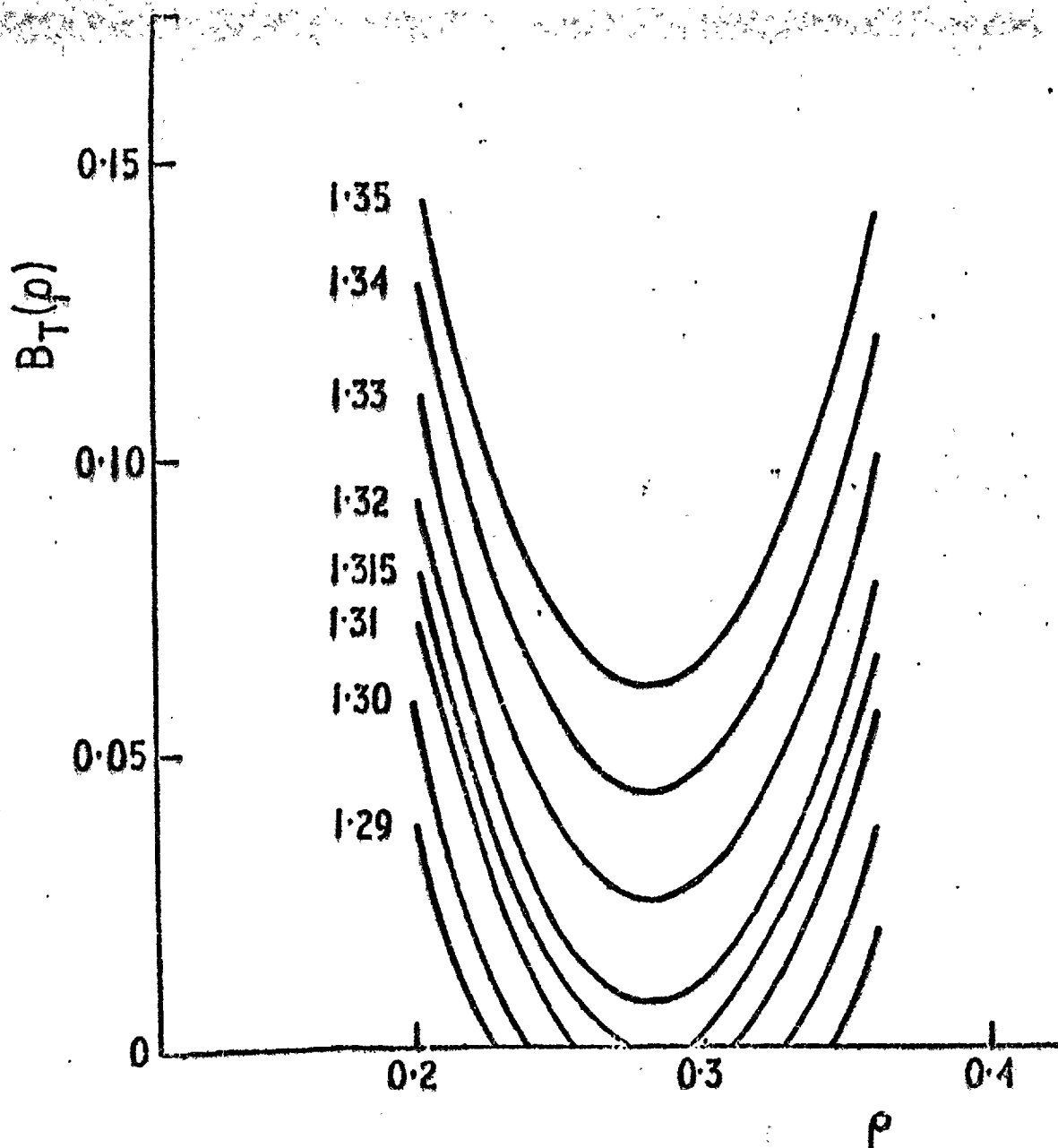


Figure 30 Isothermal bulk modulus in the critical region of a Lennard-Jones fluid. PY approximation. The curves are labelled with the reduced temperature.

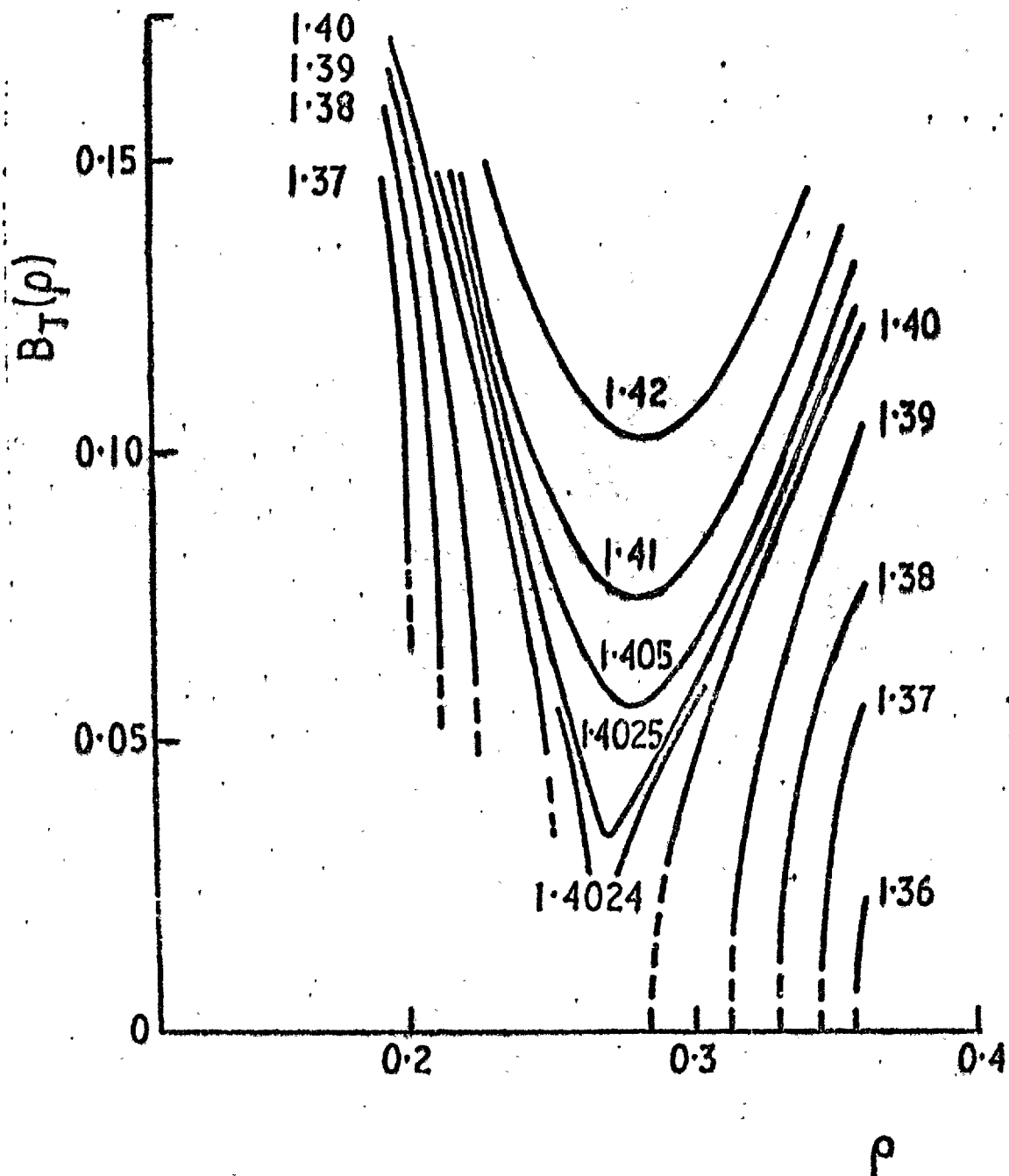


Figure 31 Isothermal bulk modulus in the critical region of a Lennard-Jones fluid. HNC approximation. The curves are labelled with the reduced temperature.

merely a subjective estimate of the interval of confidence.

Method		ρ^c	τ
Computer simulation [93]		0.32 - 0.36	1.32 - 1.36
PY (c) reference	[94]	0.278	1.315
reference	[96]	0.278	1.311
this work		0.282±0.002	1.316±0.001
	[95]		
HNC (c)reference	[95]	0.276	1.405±0.005
this work		0.265±0.005	1.4022±0.0002

Table XV Comparison of the critical parameters of several works for the PY and HNC compressibility equation of state in a Lennard-Jones fluid

Other critical exponents follow from integration of the correlation functions, but it is doubtful if enough accuracy has been reached in the critical region to withstand numerical integration. However, two exponents can be deduced from the above data. The spinodal, which reflects the same singularity as the binodal, is the locus of zeros of $B_T(\rho, \tau)$ for $\tau < \tau_c$ which were obtained from extrapolation of the subcritical isotherms (but only on the liquid side for the HNC). In both equations the spinodal is classicalm yielding an exponent β of 0.55 ± 0.05 for the PY and 0.53 ± 0.05 for the HNC.

The locus of the minima of $B_T(\rho, \tau)$ is weakly singular in both cases, but it moves in opposite directions (figure 33). The curvature of the HNC line is responsible for the low estimate of the critical density. A similar curve, but moving from the critical point to densities smaller than ρ^c , not greater, is found for the line of symmetry of the penetrable-sphere model, whose singularity is accounted by the heat capacity critical exponent [34]. From the above results it is estimated that $\alpha \approx 0$. In Table XVI the critical exponents of the PY and HNC approximations are collected.

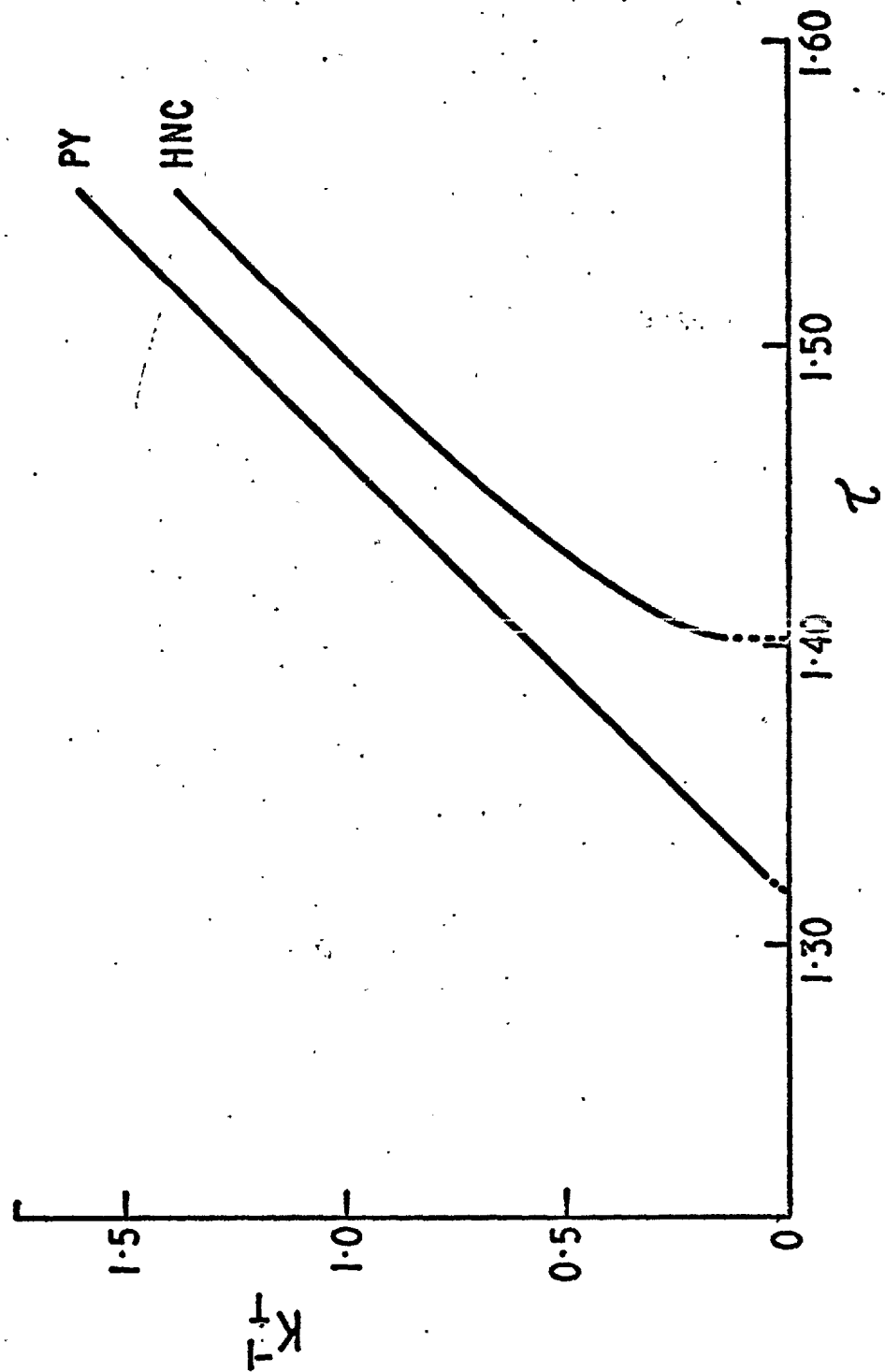


Figure 32 Isothermal bulk modulus along the critical isochores, as a function of the reduced temperature.

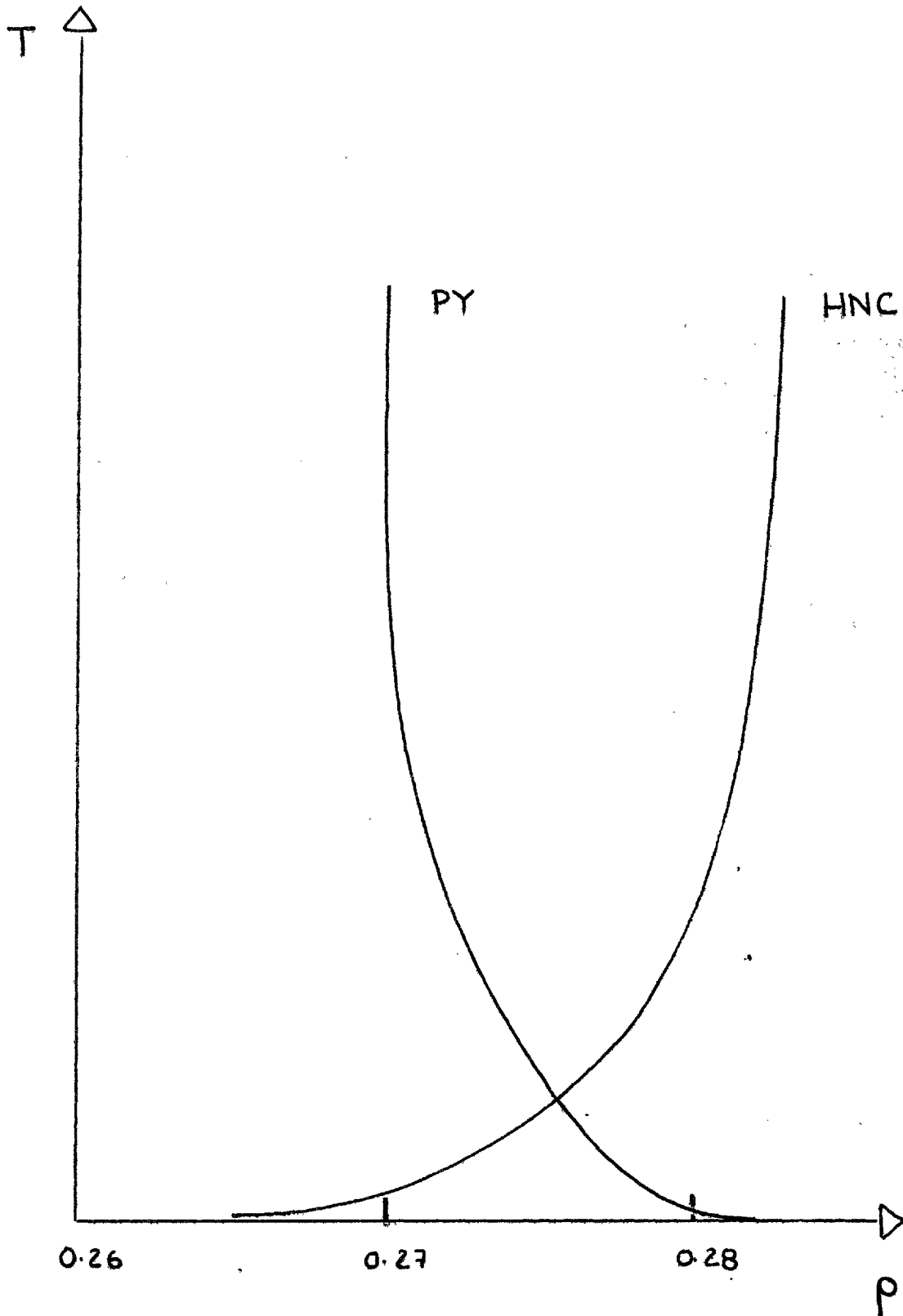


Figure 33 "Line of symmetry" , that is the locus of $(\partial B_T(\rho, T)/\partial \rho) = 0$ for the PY and HNC integral equations in a Lennard-Jones fluid near the critical point

	α	β	γ
PY	~ 0	0.55 ± 0.05	1
HNC	~ 0	0.53 ± 0.05	$\ll 1$ (0?)
Real fluid	~ 0.10	0.35	1.25

Table XVI. Critical exponents for the PY and HNC approximations in a Lennard-Jones fluid.

V.8 Discussion

The results from the first part of the chapter show a difference in the nature of the critical point predicted by the PY and HNC integral equation approximations. The former is, beyond doubt, classical while the latter, at least for the penetrable-sphere model, is non-classical. The different behaviour of the two approximations is due to the long range tail of the HNC direct correlation function and therefore should be present in a more realistic system.

In the second part the two integral equations are solved in the critical region of a Lennard-Jones fluid and their critical exponents computed. The PY equation is classical, in agreement with previous works [94,96] but the HNC although singular is unrealistic since $\gamma \ll 1$.

It is still an open question whether other approximations which are realistic and non-classical in the penetrable sphere model, e.g. PY2 [40], retain this realism in a less idealized system.

Chapter VI

SUMMARY AND CONCLUSIONS

The penetrable-sphere model of liquid-vapour equilibrium, although an idealized representation of a fluid, has been proved to be a powerful instrument for studying phase transitions and the nature of critical points.

In the original formulation the pair potentials of the binary mixture version were those of hard spheres. This limitation is not necessary. In Chapter II a generalization is discussed; any specification of the intermolecular pair potentials which leads to proper thermodynamic behaviour is equally acceptable. The one-component multibody potential is defined from the general specification of the pair potentials and its properties of short-rangedness and strong tempering depend only on the additional property of the Mayer function expressed in the inequality $0 \leq 1 + f_{ab} \leq 1$. This generalization is important because other prescriptions such as the potential of the gaussian model are more suitable for numerical work.

One interesting property of the penetrable-sphere model is the isomorphism between the one- and two- component versions. When the set of transcription rules derived from it is applied to the m -body distribution function two salient results are obtained. The one, valid in general is the equality between the one-component and the two-component all-alike distribution functions, $n^{(m)}(1, \dots, m) = n_{b, \dots, b}^{(m)}(1, \dots, m)$. The second result is peculiar to approximations such as the PY or MFA where $c_{aa} = c_{bb} = 0$ and is a simple transcription rule between the direct correlation functions of the two versions. A detailed examination can be made of the structure of the correlation functions in the neighbourhood of the critical point in the MFA as consequence of these results.

When a third species is added to the binary mixture, a three-fold symmetric ternary mixture is generated. In Chapter III and IV, the phase transitions and critical points of such mixture are discussed. Equilibria between two, three, and four phases are displayed, conforming to the pattern of "normal" phase diagrams.

In Chapter III the mean-field approximation is studied. Most results are obtained in closed form due to the relative simplicity of the model, and two phase transitions of interest are observed. The first correspond to the simultaneous vanishing of three phases in a tricritical point; four independent tricritical exponents are defined to

describe the disappearance of some order parameters. The second transition corresponds to the formation of four-phase equilibrium.

The same geometry is obtained when truncated virial expansions are considered (Chapter IV), and the MFA values of the tricritical exponents remain unchanged. This suggests that the MFA description of the tricritical singularity is correct, i.e. the tricritical point is classical. There is considerable interest to know whether this is true in general or only for a certain class of models. At the moment there is evidence supporting this and the opposite view, i.e. that tricritical points, like bicritical points, are non-classical. One model which displays non-classical. One model which displays non-classical (or anomalous) tricritical points is the Potts model.

There are several extensions of this work which seem of interest. It is intriguing why if the model described here is in some way a generalization of the Potts model to continuum systems their phase diagrams are so different. No doubt a computer experiment would be useful to decide if the normal phase diagram is indeed exhibited. For the binary mixture a molecular dynamics simulation showed the expected phase separation for high density of the two components. An extension of the model either to a quaternary mixture or to an asymmetric one would represent more closely the usual experimental situation. In the former case the task of counting the polychromatic graphs will certainly be increased, but the MFA may well be as simple and far-reaching as in the ternary mixture. The asymmetric mixture, for example, one with hard spheres of different diameter, would be a better simulation of the usual system in the laboratory. The phase diagram will surely be different from the one discussed above, and such features as the quadruple point may be absent. Such was the case in the asymmetric regular solutions of Meijering. It would also be very interesting to study a transcription, similar to that of the penetrable-sphere model, to a two-component mixture.

The nature of the bicritical points is investigated in Chapter V with the aid of the PY and HNC integral equations. For the penetrable-sphere model there is enough evidence to assert that the PY critical point is classical whereas the HNC critical point is non-classical. In the Lennard-Jones fluid a similar difference is found, although the critical point of the HNC equation is unphysical. The numerical procedure described in this chapter seems to be good enough to attempt the solution of other integral equations in the critical region; no mixing rule to ensure convergence or even to accelerate it was necessary, and the results are of accuracy comparable to previous work. The long range of the

REFERENCES

1. - T. Andrews (1869) Phil. Trans. Roy. Soc. 159, 575.
2. - J.D. van der Waals (1873) Over de Continuïteit van den Gas- en Vloeistoftoestand, Thesis, University of Leiden. English translation by R. Threlfall and J.F. Adair in Physics Memoirs 1, 333 (1890).
3. - J. S. Rowlinson (1973) Nature 244, 414.
4. - J. G. Maxwell (1875) Nature 11, 357 and 374 and J.chem.Soc, 13, 493.
5. - L. Boltzmann Lectures in Gas Theory, translated by S.G. Brush. University of California Press (1964), An historical account of the development of the gas theory and the ideas on intermolecular forces from the XVII to the XX centuries is given in S.G. Brush (1970) Arch. Rat. Mech. Anal. 39, 1.
6. M. Kac, G.E. Uhlenbeck and F.C. Hemmer (1963) J. math. Phys. 4, 216.
7. - P. Weiss (1907) J. Phys. Radium (J. de Phys, 4th series) (Paris) 6, 661.
8. - J. S. Rowlinson (1972) Ber. Bunsen Gesell. 76, 281.
9. - L. Landau and E. M. Lifshitz (1969) Statistical Physics, second edition. Pergamon Press, Oxford, Ch.14.
10. - J. D. van der Waals (1894) Z. physik Chem. 13, 657. Cited in ref.8.
11. - J. E. Verschaffelt (1907) Arch. Neerlandaises 12, 191. Cited in ref.8.
12. - M. E. Fisher (1967) Rep. Progr. Phys. 30, 615.
13. - M. von Smoluchowski (1908) Ann. Physik 25, 205.
14. - A. Einstein (1910) Ann. Physik 33, 1275.
15. - L.S. Ornstein and F. Zernike (1914) Proc. Roy.Acad. Sci. Amsterdam 17, 793.

16. - A very complete description of critical fluctuation is given in M.E. Fisher (1964) J. math.Phys. 5, 944.
17. - J.S. Rowlinson (1969) Liquid and Liquid Mixtures, second edition. Butterworths, London, Ch.8,
18. - A. Münster (1969) Statistical Thermodynamics, volume 1. Academic Press, New York and London. P. 153.
19. - P.G. de Gennes (1958) Nuovo Cim. 9, Suppl. 1, 240.
20. - R.B. Griffiths (1965) J. chem. Phys. 43, 1958.
21. - B. Widom (1965) J. chem. Phys. 43, 3898.
22. - L.P. Kadanoff (1966) Physics 2, 263.
23. - H.E. Stanley (1971) Phase Transitions and Critical Phenomena, Clarendon Press, Oxford, Ch. 11 and 12,
24. - E.A. Guggenheim (1945) J. chem. Phys. 13, 253.
25. - E. Ising (1925) Z. Physik 31, 253.
26. - R. Peierls (1936) Proc. Cambridge Phil.Soc. 32, 477.
27. - R.B. Griffiths (1964) Phys. Rev. 136, A437.
28. - L. Onsager (1944) Phys. Rev. 65, 117.
29. - C. Domb (1968) Physics Today 21, no.2, 23.
30. - T.D. Lee and C.N. Yang (1952) Phys. Rev. 87, 410.
31. - R.B. Potts (1952) Proc. Cambridge Phil. Soc. 48, 106.
32. - J.P. Straley and M.E. Fisher (1973) J. Phys. A 6, 1310.
33. - R.B. Griffiths (1974) J. chem. Phys. 60, 195.
34. - B. Widom and J.S. Rowlinson (1970) J. chem. Phys. 52, 1670.

35. - B. Widom and F.H. Stillinger (1973) J. chem. Phys. 58, 616.
36. - D. Ruelle (1971) Phys. Rev. Lett. 27, 1040.
37. - B. Widom (1971) J. chem. Phys. 54, 3950.
38. - N.D. Mermin (1971) J. chem. Phys. 54, 3958.
39. - T.J. Lie (1972) J. chem. Phys. 56, 332.
40. - T.W. Melnyk, J.S. Rowlinson and B.L. Sawford (1972) Mol. Phys. 24, 809.
41. - B.L. Sawford (1973) The Statistical Mechanics of Phase Equilibria in some Simple Model Fluids. Thesis, University of London.
42. - M. I. Guerrero, J.S. Rowlinson and B. L. Sawford (1973) Mol. Phys. 28, 1603.
43. - E. Helfand and F.H. Stillinger (1968) J. chem. Phys. 49, 1232.
44. - J.P. Straley, M.A. Cotter, T.J. Lie and B. Widom (1972) J. chem. Phys. 57, 4484.
45. - C.A. Croxton (1974) Liquid State Physics, Cambridge University Press. Ch. 2.
46. - S. Ahn (1973) Solution to the Percus-Yevick Approximation, Thesis Yeshiva University; S. Ahn and J.L. Lebowitz (1974) J. chem. Phys. 60, 523.
47. - T.W. Melnyk and J.S. Rowlinson (1971) J. comput. Phys. 7, 385 (Salsburg memorial issue),
48. - T.W. Melnyk (1973) Statistical Mechanics of some Simple Model Fluids. Thesis, University of London.
49. - T.W. Melnyk and B.L. Sawford (1975) Mol. Phys. 29, 891.
50. - (a) J.L. Meijering (1950) Philips Res. Rep. 5, 333.
(b) _____ (1951) Ibid., 6, 183.
51. - Ref. 18, p. 218.

52. - G.S. Rushbrooke and M. Silbert (1967) Mol.Phys. 12, 505.
53. - J.S. Rowlinson (1967) Mol.Phys. 12, 513.
54. - J.S. Rowlinson (1967) Disc. Faraday Soc. 43, 243.
55. - G.E. Uhlenbeck and G.W. Ford (1963) in Studies in Statistical Mechanics, vol.1, ed. by J. de Boer and G.E. Uhlenbeck, North-Holland Publishing Co. Amsterdam, Part B.
56. - B. Widom (1972) in Phase Transitions and Critical Phenomena, vol.2, ed. by C. Domb and M.S. Green, Academic Press, London, pag. 79.
57. - Handbook of Mathematical Functions, ed. by M. Abramowitz and I. Segun, Dover, New York (1965) p. 806.
58. - Ref. 57, Chapter 7.
59. - S. Ma (1973) Rev. Mod. Phys. 45, 589.
60. - G.M. Watson (1944) Theory of Bessel Functions, second edition, Cambridge University Press, p. 421.
61. - Ref. 57, p.437.
62. - Ref. 60, p. 394.
63. - B. Widom (1973) J. phys.Chem. 77, 2196.
64. - Ph. Kohnstamm (1926) in Handbuch der Physik, vol.10 (first series), ed. by H. Geiger and K. Scheele. Springer Verlag, Berlin, ch.4, p. 223.
65. - R.B. Griffiths and B. Widom (1973) Phys. Rev. A8, 2173 and references therein.
66. - E.K. Riedel and F.J. Wegner (1972) Phys. Rev.Lett. 29, 349.
67. - F.J. Wegner and E.K. Riedel (1973) Phys. Rev. B7, 248.
68. - R.B. Griffiths and J.C. Wheeler (1970) Phys. Rev. A2, 1047.
69. - J.T. Bartis (1973) J. chem. Phys. 59, 5423.

70. - J.C. Lang and B. Widom to be published.
71. - G.R. Golner (1973) Phys. Rev. B8, 3419.
72. - R.V. Ditzian and J. Oitmaa (1974) J. Phys. A7, L61.
73. - J. Sivardière and J. Lajzerowicz (1975) Phys. Rev. A11, 2101.
74. - R.J. Baxter (1973) J. Phys. C6, L445.
75. - I.G. Enting (1974) J. Phys. A7, 1617.
76. - J.P. Straley (1974) J. Phys. A7, 2173.
77. - D. Kim and R.I. Joseph (1975) J. Phys. A8, 891.
78. - D. Kim and R.I. Joseph (1975) J. Phys. A8, 905.
79. - Ref. 23 p. 89.
80. - G.S. Rushbrooke (1967) Statistical Mechanics. Clarendon Press, Oxford, p.327.
81. - G. Morrison (1975) private communication.
82. - A. Münster (1970) Classical Thermodynamics, Wiley, New York, ch. 6 and 7.
83. - J.W. Gibbs (1957) On the Equilibrium of Heterogeneous Substances, in Collected Works, vol.1, New Haven, p.129.
84. - A. Münster (1974) Statistical Thermodynamics, vol.2. Academic Press, London, pp.793 et seq.
85. - W. Murray (1972) (editor) Numerical Methods for Unconstrained Optimization, Academic Press, London.
86. - Ref. 57 p.17.
87. - H.D. Ursell (1927) Proc. Cambridge Phil.Soc. 23, 685.
88. - J.E. Mayer (1937) J. chem. Phys. 5, 67.

89. - Ref. 17 p.261; ref.18 p. 537; ref. 45 p.1; ref. 80 p. 250; and references therein. See also N.G. van Kampen (1961) *Physica* 27, 783 and W.J. Mullin (1972) *Am. J. Phys.* 40, 1473.
90. - (a) M. Bocher (1964) Introduction to Higher Algebra, Dover, New York (republication from the 1907 edition), p.124.
(b) E.W. Montroll, T.H. Berlin and T.W. Hart (1952) in *Changement de Phases*, Soc. chim. Phys. (Paris), p.211.
91. - W.G. Hoover and A.G. DeRocco (1962) *J. chem. Phys.* 36, 3141.
92. - Ref. 45 ch. 3.
93. - R.O. Watts (1973) in Statistical Mechanics, vol.1 ed. by K. Singer, The Chemical Society, London, Pag. 1.
94. - R.O. Watts (1968) *J. chem. Phys.* 48, 50.
95. - R.O. Watts (1969) *J. chem. Phys.* 50, 1358.
96. - D. Henderson and R.D. Murphy (1972) *Phys. Rev.* A6, 1224.
97. - M.I. Guerrero, G. Saville and J.S. Rowlinson (1975) *Mol.Phys.* 29, 1941.
98. - Ref. 23 p. 158.
99. - R.J. Baxter (1967) *Phys. Rev.* 154, 170; *J. chem. Phys.* 47, 4855 and (1968) *Austral. J. Phys.* 21, 563.
100. - A.A. Broyles (1960) *J. chem. Phys.* 33, 456; F. Mandel, R.J. Bearman and M.Y. Bearman (1970) *J. chem. Phys.* 52, 3315; R.J. Bearman, F. Theewes, M.Y. Bearman, F. Mandel and G.J. Throop (1970) *J. chem. Phys.* 52, 5846.
101. - J.S. Rowlinson (1966) *Mol.Phys.* 10, 533.
102. - K.E. Wilson and M.E. Fisher (1972) *Phys. Rev. Lett.* 28, 240.
103. - S. Milosevic and H.E. Stanley (1971) *J. de Phys. (Paris)* 32s, p. C1-346.
104. - P. Hutchinson and W.R. Conkie (1972) *Mol.Phys.* 24, 567.

- 105. - E. Thiele (1963) J. chem. Phys. 39, 474.
- 106. - F. Lado (1971) J. comput. Phys. 8, 417.
- 107. - L.N.G. Filon (1928) Proc. Roy. Soc. (Edinburgh) A49, 38.
- 108. - F. Mandel and R.J. Bearman (1971) J. comput. Phys. 7, 637.
- 109. - J.W. Cooley and J.W. Tukey. (1965) Math.of Comput, 19, 297.
- 110. - NAG library manual, subroutine C06AAF. Document 571, January 1973.