STATISTICAL MECHANICS OF SURFACES

by

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Abstract

Statistical Mechanics of Surfaces

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The equilibrium properties of a spherical drop are investigated using the penetrable-sphere model of a fluid. To estimate the surface tension, a new statistical mechanical formula, the extension of the Triezenberg-Zwanzig result for a planar surface, is derived. The density profiles for use in this are obtained from an integral equation expressing the constancy of chemical potential through the interface. Numerical solutions can be obtained and from these numerical estimates for the surface tension. They are in good agreement with estimates from an independent thermodynamic route. These routes, as well as a further, zero-temperature, exact, analytic one, show that the surface tension of this model increases with decreasing drop size.

The planar surface of the model is also briefly investigated using a well-known integrodifferential equation. Two approximations are made for the direct correlation function, one a systematic improvement on the other. They yield solutions for the density profile of a limited range of temperatures below the critical point. When the direct correlation function of a Lennard-Jones fluid is approximated the resulting equation for the profile resists numerical solution.

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CONTENTS

NOTATION

A number in parenthesis, eg. '(11)', in the text refers to the equation with that number in the same chapter. References to equations in other chapters include the chapter-number prefix, eg. '(6.11)'.

As explained in Chapter 5 the penetrable-sphere (ps) model exists in two equivalent versions each with its own set of variables. Equations relating the two sets of variables (transcription relations) are discussed in that chapter. Generally, the variables of the 'isomorphous mixture' version of the model are used except where the transcription is trivial as in the case of the density, ρ_α , which is often replaced by its single-component version equivalent, ρ .

Thermodynamic quantities of the penetrable-sphere model are non-dimensionalised by the use of the characteristic length, ℓ , volume v_0 and energy ε ; all the numerical results are expressed in these quantities.

List of symbols

$\mathcal{A}$	Area of a spherical surface of a drop. $\mathcal{A}_s$ is the area covered by the surface of tension.
C	Differential coefficient introduced by Gibbs to account for the curvature dependence of surfacetension (2.4)
$c(\underline{r}_1, \underline{r}_2)$	Direct correlation function between two points $\underline{r}_1$ and $\underline{r}_2$ in a fluid (that is, in general, inhomogeneous).
	Number of (ps) molecules.
p	Pressure.
$p^{\alpha,\beta}$	Function defined by (3.4). Not to be confused with p^α or p^β separately (see α,β).
R	Distance of Gibbs-surface from drop centre.
R_s	Position of the surface of tension.

R_e	Position of equimolar surface (at which the superficial density of matter vanishes).
s	Superscript indicating a superficial thermodynamic quantity, eg. n^s , the superficial density of matter (except σ_s^s , qv.).
v_0	Microscopic volume characteristic of the ps model. Equal to $4\pi \ell^3/3$ where ℓ is the ps radius. In chapters in which dimensionless units are used (eg. Chapter 9) denotes the numerical factor $4\pi/3$.
x	In Chapter 13, a dimensionless parameter which is a measure of distance from the critical point.
z	(In chapters on the planar interface) coordinate perpendicular to the surface.
α, β	Superscripts for the bulk phases - inside (α) or outside (β) the drop.
Γ	The adsorption: the superficial density of matter per unit area of Gibbs surface ($n^s/\mathcal{A}$).
δ	'Tolman's delta' - the distance separating the equimolar surface and the surface of tension (equation (2.24)).
ε	Molecular energy characterising the strength of interaction of the ps model.
$\theta(z)$	A normalised density profile function, defined by (13.2).
λ	Thermodynamic activity - $\exp(\mu/kT)$.
λ_a	Thermodynamic activity of component a of isomorphous mixture (Chapter 5).
λ_b	Thermodynamic activity of component b of isomorphous mixture. Provides a temperature scale for the (one-component) model by (5.3).
π	Pressure to temperature ratio, pv_0/kT.
$\Delta\pi$	Pressure to temperature difference across a curved surface - $(p^\alpha - p^\beta)v_0/kT$. Unchanged by transcription.
$\rho, (\rho_a)$	Dimensionless number density, Nv_0/V , in a homogeneous system. Transcription implies $N = N_a$ so ρ and ρ_a may be used interchangeably.
ρ_l, ρ_v	Liquid and vapour bulk phase densities, particularly Chapters 11, 12, 13.
σ	Differential coefficient in (2.4) identified as the surface tension at an equimolar surface. It formally depends on three quantities, eg. $\sigma = \sigma(T, R_s, R)$; partial derivatives with respect to the third are conventionally

	given a special notation: $\left(\frac{\partial \sigma}{\partial R}\right)_{T,R_s} = \left[\frac{d\sigma}{dR}\right]$ (see Chapter 2).
σ_s	Surface tension at the surface of tension (see (2.11a) and surrounding text). By (2.28) it is for practical purposes a unique surface tension for a drop of fixed size.
σ_∞	Surface tension of a planar interface.
σ_s^T	A value of σ_s deduced from thermodynamic arguments (Chapter 10).
σ_s^S	A value of σ_s deduced from the formula derived in Chapter 4 (Chapter 10).
σ^* (σ_a^*)	An effective density introduced for a planar surface in Chapter 6 and derived for a spherical surface in Chapters 7 and 8. Many surface quantities may be obtained in terms of it, eg. (6.5), (7.8), (7.9). The corresponding quantities in the one- and two- component versions of the model, σ^* and σ_a^* can be used interchangeably because $\rho_a = \rho$ by transcription.
σ_b^*	An effective density, the counterpart to σ_a^* in the two-component version of the ps model (eg. (8.10)).
ϕ	Dimensionless energy density - $\frac{u\, v_0}{V \varepsilon}$.
ω	The solid angle subtended by the conical section of a drop (Figure 2) analysed in Chapter 2.

CHAPTER 1 INTRODUCTION

This chapter takes the form of an overview; it outlines the scope and aims of later ones. The whole work is concerned with the liquid-vapour interface and nearly all of it with a particular model, the penetrable-sphere model (Chapter 4 and 14 provide the main exceptions). Within these limits the work falls into two parts: up to Chapter 10 the spherically curved surface is considered, after that the planar surface is investigated from a new perspective. Background theory for both parts is combined in Chapters 2 to 6.

The classical thermodynamic theory of systems with a spherical interface ("drops") is described in Chapter 2. The Gibbsian scheme, which has earned almost universal acceptance, is used. Only a small number of essential results are obtained, particularly the Tolman equation (Tolman, 1949) for the variation of surface tension with drop size.

Chapter 3 is a selective account of important results in the microscopic theory of surface tension. A great deal of important analysis since the pioneering work of Kirkwood and Buff (1949) has been expressed in terms of the variation of the pressure tensor through the interface. Only a brief outline of this is given, however, because the parallel theory in terms of the direct correlation function is more useful in applications to the penetrable-sphere model. The important results of this theory are noted.

In Chapter 4 a new general formula for the surface tension of spherically curved surfaces is derived. In its form it is a generalisation of the Triezenberg-Zwanzig (1972) formula for the surface tension of a planar interface although the derivation given here follows that of Lovett, Dehaven, Vieceli and Buff (1973) more closely. Later this formula is tested by applying it to a penetrable-sphere model drop.

Chapter 5 is the first of two chapters devoted to a description of the penetrable-sphere model (Widom and Rowlinson, 1970). In it the version used later is specified (a considerable number have been used, respresenting not only pure fluids, but also several-component mixtures). The model can be described in two mathematically equivalent ('isomorphous') ways, one of which has all the properties of a two-component mixture apart from a temperature variable. This is the "isomorphous mixture" which is used in most of the subsequent chapters because the equations take on a much simpler form than the equivalent "one-fluid" description, as this chapter explains. Finally, an explicit formula for the direct correlation function (dcf) of the model is given which is valid both in homogeneous and interfacial regions. This formula is used repeatedly in later chapters.

Chapter 6 covers the application of statistical mechanics to the planar interface of the penetrable-sphere model. This is largely the work of Leng, Rowlinson and Thompson (1976, 1977). Much of the analysis of the spherical surface of the model has an essential basis in the ideas described in this chapter.

Chapter 7 is the first of three chapters which end in the structure of a penetrable-sphere model drop being obtained for the first time. In this one we find the bulk phase densities which are in thermal and chemical equilibrium in the presence of a curved surface. The general form of the equation for the density profile is deduced together with some limits which it must yield, but the detailed form of the equation is left until the following chapter.

The density profile is shown to be the solution of a pair of simultaneous, non-linear integral equations in Chapter 8. Solution of these equations proves to be a complex task, a description of which occupies most of the remainder of this chapter. The numerical solutions which are finally obtained are found to differ qualitatively very little from planar profiles at the same temperature. Quantitatively, however, this difference proves to be crucial for estimating the curvature dependence of the surface tension.

In Chapter 9 two results of the direct-correlation-function theory of liquid surfaces are used. The first of these is an integrodifferential equation for the density profile (used again in Chapters 11 to 14). This is shown to lead to the same equation for the density profile as that used in Chapter 8, which was obtained by arguments special to the penetrable-sphere model. The other result is the surface tension formula of Chapter 4. With the known result for the dcf of the model in terms of the density, this leads - after a considerable amount of algebraic simplification - to an expression for the surface tension in terms of the density profiles.

The surface tension, as a function of drop size, is obtained in Chapter 10 using the results of the previous two chapters. It is also shown that the surface tension can be obtained from thermodynamics alone provided that the distribution of matter in the interface and the pressures in the homogeneous phases on each side of it are known. Both these surface tensions are valid only up to the leading asymptotic correction to the planar surface tension. To this order, and to within numerical uncertainty, they agree. They also agree with an analytic zero-temperature result which, moreover, is independent of the mean-field approximation used for the numerical calculations. The results of this chapter show that the effect of curvature on surface tension of penetrable-sphere model drops is slight (~ 5% for drops of radius 10 atomic diameters) and such as to increase it.

Attention is re-focussed on the planar surface in Chapter 11. This is well understood for the penetrable-sphere model in a mean-field approximation (Leng, Rowlinson and Thompson, 1976, 1977) which makes it ideal for testing approximate theories (eg. Harrington and Rowlinson, 1979; Hemingway, Rowlinson and Severin, 1980). In this and the following chapters an approximate equation for the density profile is deduced. A very simple ansatz for the interfacial direct correlation function (idcf) is constructed using only the density profile and the dcfs appropriate to the coexisting bulk phases. The attraction of this form is that the full idcf, while available for this model, is in general inaccessible whereas the bulk phase dcfs are readily available from experiment and a number of accurate and well-tested theories.

In Chapter 12 the equation for the density profile which uses the ansatz of the previous chapter is obtained and a numerical method for solving it devised. This proves to be successful near the critical point, where the ansatz is expected to be most accurate, but fails at lower temperatures. This behaviour is traced to an 'inconsistency' in the use of the ansatz which treats the bulk phase densities as known a priori in an equation in which they are not.

Chapter 13 uses Henderson-Lekner type sum-rules (Henderson and Lekner, 1980) to remove this inconsistency and thus considerably extends the range of temperature for which satisfactory density profiles can be obtained from this approach. Unfortunately, this technique is not of very general application (and cannot, for example, be used for the Lennnard-Jones fluid treated in Chapter 14) as it requires (a moment of) the bulk phase dcf to be known as an expansion about the critical point.

Chapter 14 repeats the analysis of Chapters 11 and 12 for a Lennard-Jones fluid. Although all the input quantities are known (or can be readily approximated) for this model the resulting equation is not soluble by the algorithm which was used with (limited) success on the penetrable sphere model. This is almost certainly due to the shortcoming of the general form of the ansatz found in the earlier chapter.

Overall, from the first part of the work a fairly detailed picture of the structure and thermodynamics of the spherical surface of a simple model fluid emerges. This confirms the essential correctness of a new generalisation to spherical surfaces of the Triezenberg-Zwanzig (1972) surface tension formula. This is believed to be the first (numerical) proof of the consistency of statistical mechanics and thermodynamics for the surface tension of the curved surface of any model.

The work on the planar surface shows that the Lovett-Mou-Buff (1976) equation can be used in conjunction with a crude ansatz for the correlation function to produce acceptable density profiles, at least in the case of the penetrable-sphere model. No comparable use of the equation for other models is known, although the first member of the BGY hierarchy, which is an integro-differential equation of similar form, has been used in this way by a number of workers (see Chapter 12 for references).

CHAPTER 2 THERMODYNAMICS OF DROPS

This chapter covers the basic classical thermodynamics of spherical, one-component, two-phase systems ("drops"). The treatment is essentially that of Gibbs (1928) as developed by Tolman (1949). The theory has also been set out very concisely by Buff (1951). We start, however, by giving a simple derivation of Laplace's formula for the difference in pressure across a curved surface.

It has been known for a long time that, to a good macroscopic approximation, the surface of a liquid behaves like a thin, uniformly stretched membrane. If the surface in Figure 1 may be treated as such a membrane, with tension σ_s per unit length, then the principle of virtual work tells us that

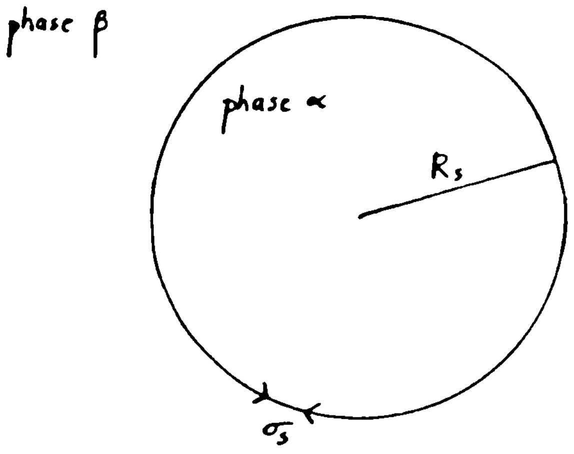
$$\sigma_s \, d\mathcal{A}_s - (p^\alpha - p^\beta)\, dV^\alpha = 0 \qquad (2.1)$$

Here $\mathcal{A}_s$ is the area of the surface at R_s ($\mathcal{A}_s = 4\pi R_s^2$), V^α is the volume enclosed by this surface and p^α and p^β are the interior and exterior pressures respectively. Expressing $d\mathcal{A}_s$ and dV^α in terms of a change in R_s in (1) gives the well-known Laplace equation

$$p^\alpha - p^\beta = \frac{2\sigma_s}{R_s} \qquad (2.2)$$

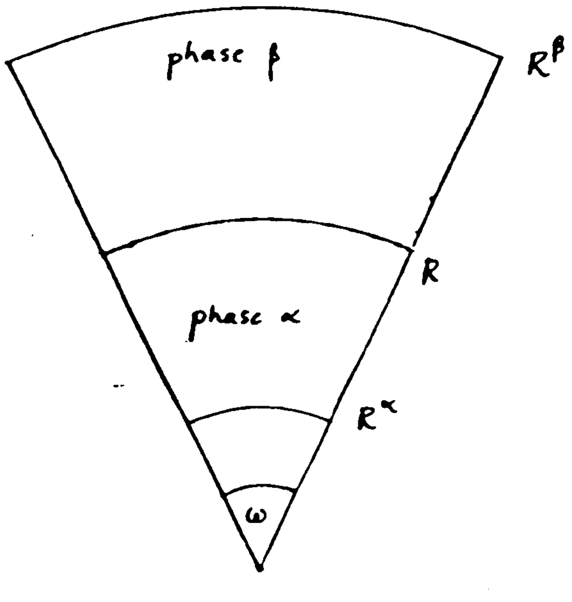
On a microscopic scale difficulty can be experienced in unambiguously defining the quantities on the right-hand side of (2). Gibbs (1928, p.219) dealt with these by introducing the hypothetical dividing surface known by his name. For a drop this is a spherical surface of arbitrary radius centred on the

Figure 1. Macroscopic view of a drop



The drop of liquid (phase α) is separated from its vapour (phase β) by a spherical surface of radius R_s . This is the surface of tension, in which the surface tension acts It is a tangential force of magnitude σ_s per unit length of great circle.

Figure 2. The thermodynamic system



Here the system is bounded by spherical surfaces of radius R^α and R^β , and walls normal to these surfaces which enclose a solid angle ω . All the walls are ideal and introduce no additional inhomogeneity. The Gibbs surface at (arbitrary) position R defines the extent of the phases.

centre of mass of the drop; it is a surface of constant density.

The Gibbs surface enables us to associate extensive quantities, like energy, entropy and amount of matter, with the surface. Thus the superficial energy, E^s, will be defined by

$$E^s = E - E^\alpha - E^\beta \tag{2.3}$$

E is the energy of the whole system, and E^α and E^β are the energies which the two phases α and β would have if they coexisted homogeneously up to the Gibbs dividing surface (they are thus given by the product of V^α and V^β with the appropriate bulk energy densities). It is convenient to consider a conical section of a spherical system as in Figure 2 with ideal radial walls enclosing a solid angle ω.

Gibbs reasoned that a spherical fluid system with an interface would have a free energy with the following contributions: a 'chemical' term μdn, mechanical work terms $p^\alpha dV^\alpha$ and $p^\beta dV^\beta$ and a term which is proportional to the change in area <u>of the Gibbs surface</u>. Because this will usually not be at R_s (equation (1)) an extra term, CdR, is required leading to

$$dF = -SdT - p^\alpha dV^\alpha - p^\beta dV^\beta + \sigma d\mathcal{A} + C\,dR + \mu dn \tag{2.4}$$

The quantities V^α, V^β, $\mathcal{A}$, n and F in equation (4) are homogeneous functions of order unity of the solid angle, ω (which is proportional to the volume of the whole system). They are thus the surface analogues of extensive variables; (4) may be integrated in the usual way:

$$F = -p^{\alpha}V^{\alpha} - p^{\beta}V^{\beta} + \sigma\mathcal{A} + \mu n \qquad (2.5)$$

If we imagine a small change in the value of R at constant ω, we obtain from (4)

$$dF = -(p^{\alpha} - p^{\beta})\omega R^{2} dR + \sigma 2\omega R dR + C dR \qquad (2.6)$$

An equivalent result may be obtained by formally differentiating (5) with respect to R :

$$dF = \left\{ -(p^{\alpha} - p^{\beta})\omega R^{2} + \sigma 2\omega R + \omega R^{2}\left[\frac{d\sigma}{dR}\right] \right\} dR \qquad (2.7)$$

Here the conventional notation (Ono and Kondo, 1960) to indicate a partial derivative with respect to the Gibbs surface alone is used. Comparison of (6) and (7) yields

$$\frac{C}{\mathcal{A}} = \left[\frac{d\sigma}{dR}\right] \qquad (2.8)$$

An important feature of the Gibbs surface is that its position is completely arbitrary and does not affect the physical state of the system; thus, $[dF/dR] = 0$ in both (6) and (7). This result provides two generalised Laplace equations:

$$p^{\alpha} - p^{\beta} = \frac{2\sigma}{R} + \frac{C}{\mathcal{A}} \qquad (2.9)$$

$$p^{\alpha} - p^{\beta} = \frac{2\sigma}{R} + \left[\frac{d\sigma}{dR}\right] \qquad (2.10)$$

When the Gibbs surface is coincident with the special surface, the surface of tension, used in equation (1) and Figure 1, we have

$$\sigma(R_s) = \sigma_s \tag{2.11a}$$

$$\frac{C}{\mathcal{A}_s} = \left[\frac{d\sigma}{dR}\right]_{R=R_s} = 0 \tag{2.11b}$$

where we have made the dependence of σ on R explicit.

We now look at the superficial free energy; by definition

$$dF^s = dF - dF^\alpha - dF^\beta \tag{2.12}$$

which on introducing (4) becomes

$$dF^s = -S^s dT + \sigma d\mathcal{A} + C dR + \mu dn^s \tag{2.13}$$

From this we may identify σ as the partial derivative

$$\sigma = \left(\frac{\partial F^s}{\partial \mathcal{A}}\right)_{T, R, n^s} \tag{2.14}$$

When R is chosen so that n^s vanishes (when it has the value R_e), by the arguments used to obtain (5)

$$\sigma = \frac{F^s}{\mathcal{A}} \tag{2.15}$$

This particular Gibbs surface is known as the equimolar surface. Equations (3) and (5) may be used directly for F^s :

$$dF^s = \sigma\, d\mathcal{A} + \mathcal{A}\, d\sigma + \mu\, dn^s + n^s d\mu \qquad (2.16)$$

This can be used with (13) to derive a surface version of the Gibbs-Duhem equation:

$$C\,dR = S^s dT + \mathcal{A}\, d\sigma + n^s d\sigma \qquad (2.17)$$

For a general isothermal change we have

$$\left(\frac{\partial \sigma}{\partial R}\right)_T = \frac{C}{\mathcal{A}} - \frac{n^s}{\mathcal{A}}\left(\frac{\partial \mu}{\partial R}\right)_T \qquad (2.18)$$

The combination $n^s/\mathcal{A}$ is called the adsorption and is given the symbol Γ and an appropriate suffix. When $R = R_s$ we have Γ_s which is given by (18) and (11b)

$$\left(\frac{\partial \sigma_s}{\partial \mu}\right)_T = -\Gamma_s \qquad (2.19)$$

Tolman in 1949 showed how this equation could be used to obtain the variation of σ_s with R_s. First, Gibbs-Duhem equations for the bulk phases are used to eliminate the chemical potential, μ :

$$d\mu = \frac{dp^\alpha}{\rho^\alpha} = \frac{dp^\beta}{\rho^\beta} \qquad (2.20)$$

(Note that we have only associated a chemical potential with phases α and β and the whole system - never with the surface itself).

Laplace's equation, (2), may be written

$$dp^{\alpha} - dp^{\beta} = d\left(\frac{2\sigma_s}{R_s}\right) \qquad (2.21)$$

and combined with (20) and (21) to yield

$$\left(\frac{\partial \sigma_s}{\partial(2\sigma_s/R_s)}\right)_T = \frac{-\Gamma_s}{\rho^{\alpha} - \rho^{\beta}} \qquad (2.22)$$

This is a differential equation which gives the variation of a surface tension, σ_s , with R_s which, macroscopically at least, is the position of the physical surface. This variation is much more useful than the variation with R , the position of the Gibbs surface since this may be placed arbitrarily.

The adsorption, Γ_s , may be related to R_s and R_e by simple geometry:

$$\Gamma_s = (\rho^{\alpha}-\rho^{\beta})\,\delta\left(1 + \frac{\delta}{R_s} + \frac{1}{3}\frac{\delta^2}{R_s^2}\right) \qquad (2.23)$$

where δ is defined by

$$\delta = R_e - R_s \qquad (2.24)$$

and is a length of microscopic (molecular) dimensions.

In fact, as Tolman pointed out, for drops which are large enough to have a thermodynamically well-defined interior phase, α , δ will be a very slowly varying function of R_s and may be replaced in (20) by its limiting value, δ_∞ , where

$$\delta_\infty = \mathop{\mathrm{lt}}_{R_s \to \infty} (R_e - R_s) \qquad (2.25)$$

Although a complete solution to (22) may be obtained, eg. Nonnemacher (1977), in the range of drop sizes for which the substitution $\delta = \delta_\infty$ is adequate, a series solution in (δ_∞/R_s) taken to first order,

$$\sigma_s = \sigma_\infty\left(1 - \frac{2\delta_\infty}{R_s}\right) + O\left(\frac{\delta_\infty}{R_s}\right)^2 \qquad (2.26)$$

(where $\sigma_\infty = \lim_{R_s \to \infty} \sigma_s$) will be sufficient for all thermodynamically significant variations.

The quantity σ_s , which appeared originally in the Laplace equation (2), in the above equation may be thought of as a 'mechanical' surface tension. The 'thermodynamic' surface tension, σ , differs from σ_s in that it has an unphysical feature - its value depends on the position of a purely nominal Gibbs dividing surface, R . The actual dependence can be obtained by substituting Laplace's equation, (2), which defines σ_s/R_s , into (7):

$$\frac{2\sigma_s}{R_s} = \frac{2\sigma}{R} + \left[\frac{d\sigma}{dR}\right] \qquad (2.27)$$

Equation (27) has the solution

$$\frac{\sigma(R)}{\sigma_s} = 1 + \frac{(R-R_s)^2}{R^2}\left(\frac{R_s + 2R}{3R_s}\right) \qquad (2.28)$$

This equation confirms the implication of (11b) that σ has a turning point at R_s . From (28) the departure of $\sigma(R)$ from its minimum value, σ_s , will be only of order R_s^{-2} Clearly, whenever the Gibbs surface is within a microscopic distance of the surface of tension at R_s , and certainly when

$R = R_e$, the surface tension, σ , will be essentially independent of R and equal to σ_s given by (26). We may, therefore, in succeeding chapters talk of 'the surface tension' without reference to any dividing surface and without distinction between the 'thermodynamic' surface tension, σ , and the 'mechanical' surface tension, σ_s .

However, once we go to drop sizes for which R_s^{-2} is not a negligible quantity, this situation changes dramatically. The thermodynamic surface tension becomes unphysical, being no longer sensibly independent of R . Moreover, the dependence of δ on R_s will become non-negligible, preventing any solution to (22), and certainly invalidating the asymptotic result (26). Physically, for drops of a very small radius the interior phase, α , will cease to be homogeneous even at the centre. At this limit the above thermodynamic formalism, which assumes that α may be treated as a homogeneous phase, breaks down completely. The mechanical surface tension, σ_s , of Laplace's equation becomes undefined also because the pressure in the interior phase, p^{α} in (2), will no longer be a simple scalar quantity.

Thus, a unique surface tension of a drop, σ or σ_s , is defined by thermodynamics by (26) or its alternative form

$$\sigma_s = \sigma_\infty \left(1 - \frac{2\delta_\infty}{R_e}\right) + 6\left(\frac{\delta_\infty}{R_s}\right)^2 \qquad (2.29)$$

only up to a first order correction to its value for a drop of infinite size, σ_∞ . Attempts to obtain the surface tension by the methods of statistical mechanics, we shall find, suffer from the same restriction, which might be expected of a theory which is exact only in the thermodynamic limit. We expect, however, that (26) and the equivalent statistical mechanical results will be practically useful for moderate sized drops. This is confirmed by the results for the model system presented later.

CHAPTER 3 THEORY OF SURFACE TENSION

It is only possible in this outline to state a few useful results and give an indication of how they are derived. Fortunately however, a number of excellent reviews exist (Ono and Kondo, 1960; Evans, 1979; Rowlinson and Widom, 1982) which together give a wide-ranging coverage of the theory of interfaces of simple fluids.

The work of Kirkwood and Buff (1949) served as the starting point for a very detailed development of the theory of both planar and spherical interfaces, particularly for systems which interact via pair potentials. A number of papers in the early 1970's provided a parallel treatment in terms of the direct correlation function which is particularly useful in treating systems, like the penetrable-sphere model, which interact via a multibody potential.

Kirkwood and Buff (1949) obtained an expression for the surface tension in terms of the stress transmitted across a unit hypothetical strip perpendicular to a planar interface. In doing this they implicitly use the result

$$\sigma_s = \int_{-\infty}^{\infty} dz \, [p^{\alpha,\beta} - p_T(z)] \qquad (3.1)$$

which Ono and Kondo (1960) attribute to Bakker (for a derivation see Navascues, 1979). In this equation $p^{\alpha,\beta}$ is the common value of the scalar pressure in the two homogeneous phases and $p_T(z)$ is the magnitude of the component of the pressure tensor tangential to the interface. An alternative route (Buff, 1952) is to use the thermodynamic identity (2.14):

$$\sigma_s = \left(\frac{\partial F^s}{\partial \mathcal{A}} \right)_{T,R,n^s} \qquad (3.2)$$

which for a planar interface is independent of position of the Gibbs surface. The superficial free energy in (2) may be obtained in terms of the canonical partition function and hence the distribution functions. The final result is equivalent to that obtained from (1).

These arguments may be extended to drops. The mechanical arguments that lead to (1) for a planar surface lead to

$$\sigma_s = \frac{1}{R_s} \int_{R^\alpha}^{R^\beta} dr \, r \left[p^{\alpha,\beta}(r; R_s) - p_T(r) \right] \qquad (3.3)$$

for a curved surface (see Figure 2). Now $p^{\alpha,\beta}$ no longer has a single value as in (1), but is defined by

$$p^{\alpha,\beta}(r; R) = \begin{cases} p^\alpha & (r < R) \\ p^\beta & (r \geqslant R) \end{cases} \qquad (3.4)$$

The position, R_s , of the surface of tension may also be obtained in terms of $p_T(r)$ in this analysis. It is the position where the effective force produced by the hypothetical membrane must act to balance moments in the system

$$R_s = \frac{\int dr \, r^2 \left[p^{\alpha,\beta}(r; R_s) - p_T(r) \right]}{\int dr \, r \left[p^{\alpha,\beta}(r; R_s) - p_T(r) \right]} \qquad (3.5)$$

A complete treatment of the spherical case was provided by Buff (1955). He took as his starting point the force balance equation of hydrostatics which, for equilibrium in the absence of an external field may be written

$$\underline{\nabla} \cdot \underline{\underline{p}}(\underline{r}) = \underline{0} \qquad (3.6)$$

Here $\underline{\underline{p}}$ is the pressure tensor at a point $\underline{r}$ in the system. In a system with spherical symmetry, it has two independent components, $p_N(r)$ and $p_T(r)$, and may be written in terms of the unit dyadics $\hat{\underline{r}}\hat{\underline{r}}$, $\hat{\underline{\theta}}\hat{\underline{\theta}}$ and $\hat{\underline{\phi}}\hat{\underline{\phi}}$:

$$\underline{\underline{p}}(\underline{r}) = p_N(r)\,\hat{\underline{r}}\hat{\underline{r}} + p_T(r)[\hat{\underline{\theta}}\hat{\underline{\theta}} + \hat{\underline{\phi}}\hat{\underline{\phi}}] \tag{3.7}$$

Equation (6) then leads to a relationship between $p_N(r)$ and $p_T(r)$ which may be written

$$\frac{d}{dr}[p_N(r)\,r^2] = r\,[p_N(r) + 2p_T(r)] \tag{3.8}$$

With the introduction of $p^{\alpha,\beta}(r;R)$ from (4) an integration leads to an expression for $p^\alpha - p^\beta$,

$$\begin{aligned} p^\alpha - p^\beta = {} & \frac{2}{R^3}\int_0^\infty dr\, r^2[p^{\alpha,\beta}(r;R) - p_T(r)] \\ & - \frac{2}{R^3}\int_0^\infty dr\, r(r-R)[p^{\alpha,\beta}(r;R) - p_T(r)] \end{aligned} \tag{3.9}$$

This may be compared with the equation of thermodynamics (2.10); the first term on the right-hand side of (9) may be identified with $\sigma(R)$ and the second with $[d\sigma/dr]$. With this result Buff (1955) was able to put the whole of the thermodynamic theory of Chapter 2 on a microscopic basis. This argument from hydrodynamics is, to terms of thermodynamic significance ($O(R_s^{-1})$), equivalent to the above argument from mechanics (Rowlinson and Widom, 1982, Chapter 4), although one small defect remains which is noted below.

The above results for the surface tension and the surface of tension can be cast in terms of the interaction potential by using an appropriate statistical mechanical expression for the components of the pressure tensor. Irving and Kirkwood (1950) obtained such an expression for a system of pair potentials. As they, and other authors, notably Harasima (1958), noted this expression is not unique. Although the non-uniqueness does not affect the value of the surface tension, different choices for the expression for the pressure tensor do lead to uncertainties in the values of the surface of tension from (5). The situation has been recently reappraised by Schofield and Henderson (1982) who obtain a completely general expression for the pressure tensor which contains a line integral whose path may be chosen arbitrarily. The consequences of this arbitrariness for the thermodynamics of drops have been examined by these authors (Henderson and Schofield, 1982). They conclude that the ambiguity in the position of the surface of tension from an equation such as (5) is genuine, but that this does not prevent asymptotic expansions of the form (2.26) being well-defined. This has been interpreted as being due to the breakdown of essentially macroscopic moment-balance arguments in systems of molecular dimensions (Rowlinson and Widom, 1982; see also Hemingway, Henderson and Rowlinson, 1982).

The original result of Kirkwood and Buff (1949) was for a system of pair potentials. These are still the only systems for which calculations are available although the route can formally be extended to multibody potentials. The direct correlation function (dcf) expression for the surface tension of a planar surface (Triezenberg and Zwanzig, 1972) is computationally convenient and independent of the interaction potentials, and has been shown to be equivalent to the earlier route (Schofield, 1979). It is therefore to be much preferred for the penetrable-sphere model which has a complex multibody potential. In Chapter 4 the route is generalised to a spherical interface. Unfortunately the components of the pressure tensor are not given and so equation (5) cannot be tested (although the surface of tension can be readily calculated using the Laplace equation - this shows no evidence of being ill-defined).

An equation for the density profile in terms of the dcf is also available (Lovett, Mou and Buff, 1976: Wertheim, 1976). It is both independent of the interaction potential <u>and</u> the geometry of the system. (It is the analogue of the first member of the BGY hierarchy (see, for example, Toxvaerd, 1975) for pair potential systems). In Chapter 9 this equation is used for the spherical density profile of a penetrable-sphere model fluid which is itself used later in the calculation of the surface tension using the dcf route described above.

CHAPTER 4 DIRECT CORRELATION FUNCTION EXPRESSION FOR THE SURFACE TENSION OF A DROP

In the last chapter the advantage (for application to the penetrable-sphere model) of the Triezenberg-Zwanzig (1972) route to the surface tension, that it was independent of the form of the interaction potential, was explained. In its original form, however, it is restricted to planar surfaces; it is the purpose of this chapter to present a derivation which extends it to spherical surfaces. The method is based on the derivation of the Triezenberg-Zwanzig result by Lovett, Dehaven, Vieceli and Buff (1973) by applying a force balance condition to the infinitesimal bending of a planar surface. The result appears in Hemingway, Henderson and Rowlinson (1982); alternative derivations appear in Henderson and Schofield (1982).

We consider the application of an external field which 'bends' a spherical interface about its equimolar surface. The choice of the equimolar surface is arbitrary but convenient as it is this surface whose position is determined by the distribution of matter in the interface - it is certainly the natural choice for a stepfunction interface. This arbitrariness is believed to affect the final result only to terms of order R_e^{-2}. For a small external field the only effect will be to bodily shift the density profile through a distance ΔR_e. For this reason, in this chapter (and this chapter only) we work with a density profile $\rho(r')$ where r' is a radial distance measured from the equimolar surface.

The change in density, $\Delta\rho(\underline{r})$ at a point $\underline{r}$ arising from the displacement of the equimolar surface, ΔR_e, will be given by

$$\Delta\rho(\underline{r}) = \rho\left([x^2+y^2+(R_e+\Delta R_e+z)^2]^{1/2} - [R_e+\Delta R_e]\right) - \rho\left([x^2+y^2+(R_e+z)^2]^{1/2} - R_e\right) \tag{4.1}$$

using the co-ordinate system shown in Figure 3. A Taylor expansion of the density profile about $r \equiv \left([x^2+y^2+(R_e+z)^2]^{1/2} - R_e\right)$ then yields

$$\Delta\rho(\underline{r}) = -\frac{(x^2+y^2)}{2R_e^2}\Delta R_e \frac{d}{dr}\rho(r) + \mathcal{O}\left(\frac{1}{R_e}\right)^3 \tag{4.2}$$

The external field $v(r)$ required for this derivation is by definition

$$v(\underline{r}_1) = \int d\underline{r}_2 \left(\frac{\delta v(\underline{r}_1)}{\delta\rho(\underline{r}_2)}\right)\Delta\rho(\underline{r}_2) \tag{4.3}$$

Following Lovett et al., we introduce the second Yvon equation

$$\frac{\delta v(\underline{r}_1)}{\delta\rho(\underline{r}_2)} = kT\left(c(\underline{r}_1,\underline{r}_2) - \frac{\delta(\underline{r}_1-\underline{r}_2)}{\rho(\underline{r}_1)}\right) \tag{4.4}$$

The excess pressure across the interface is, from hydrodynamics,

$$\Delta p = \int_{-\infty}^{\infty} dz\, \rho(z)\, \frac{\partial v}{\partial z}(0,0,z) \tag{4.5}$$

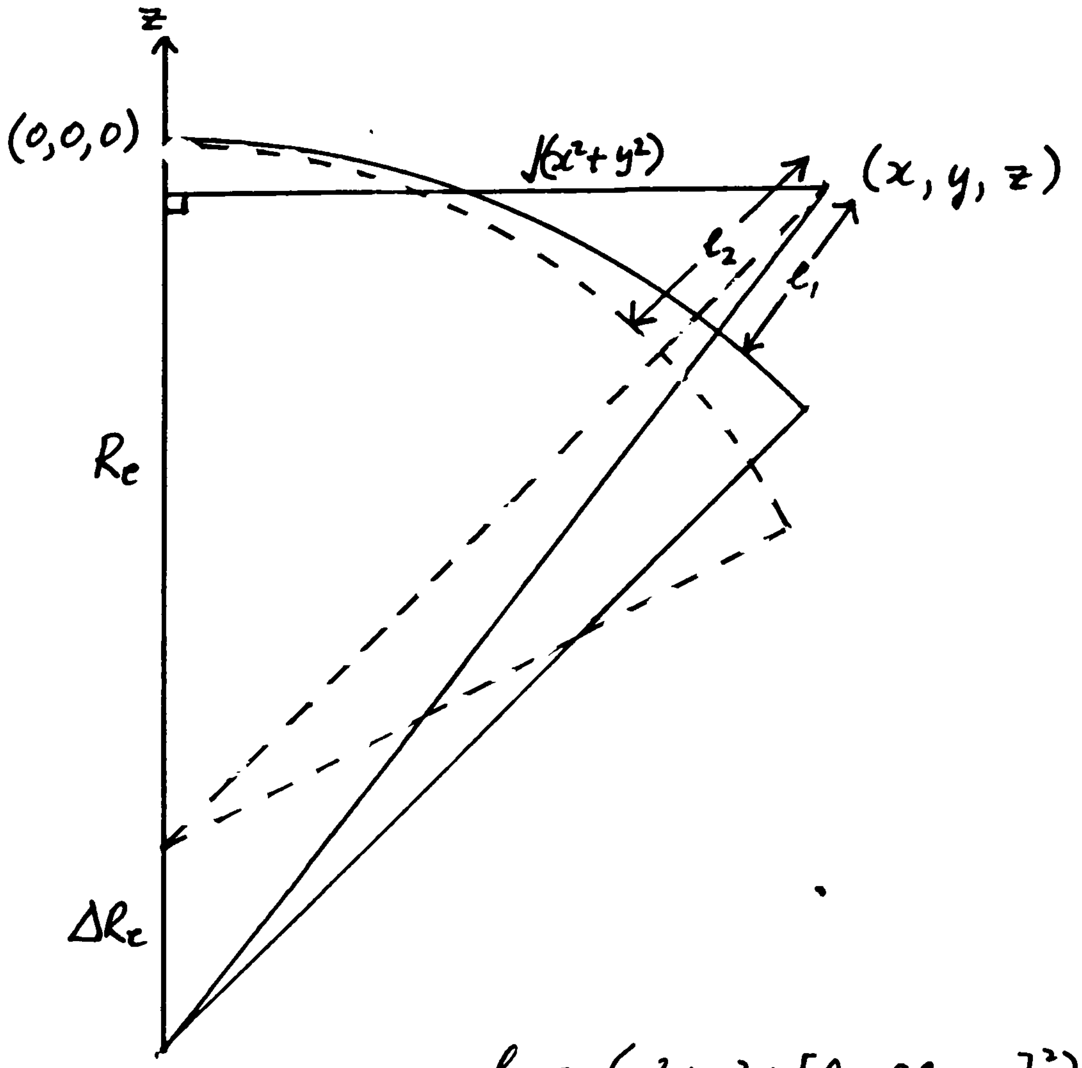
which becomes

$$\Delta p = \int_{-\infty}^{\infty} dz\, \frac{d\rho(z)}{dz}\, v(0,0,z) \tag{4.6}$$

provided the field vanishes in the bulk phases.

Rewriting Δp as $p^\alpha - p^\beta$ and taking the limit $\Delta R_e \to 0$

Figure 3. Bending of a spherical interface.



$$\ell_1 = (x^2+y^2+[R_e+\Delta R_e+z]^2)^{1/2} - (R_e+\Delta R_e)$$

$$\ell_2 = (x^2+y^2+[R_e+z]^2)^{1/2} - R_e$$

The figure shows the drop before (continuous lines) and after (dashed lines) the distortion described in the text. The key quantity in deriving the surface tension formula is the change in density at the point (x,y,z) which results. It depends on the two distances from the equimolar surfaces, ℓ_1 and ℓ_2 which are illustrated.

after substituting (2), (3) and (4) into (6) we have

$$\frac{d}{dR_e^{-1}}\left(p^\alpha - p^\beta\right) = kT\int_{-\infty}^{\infty} dz_1\, \rho(z_1) \int d\underline{r}_2\, c(\underline{r}_1,\underline{r}_2) \times \times \left(x_{12}^2 + y_{12}^2\right) \rho'(r_2) \qquad (4.7)$$

In order to obtain the surface tension we rewrite the left-hand side of (7) identically,

$$\frac{d}{dR_e^{-1}}\left(p^\alpha - p^\beta\right) = \left(\frac{R_e}{R_s}\right)^2 \left(\frac{dR_s}{dR_e}\right) \frac{d}{dR_s^{-1}}\left(p^\alpha - p^\beta\right) \qquad (4.8)$$

in which the last factor can readily be estimated from the Laplace equation (2.2). The surface of tension and the equimolar surface will move together to at least first order so $\frac{dR_s}{dR_e}$ is unity. Introducing Tolman's equation (2.26) for the surface tension, (8) becomes

$$\frac{d}{dR_e^{-1}}\left(p^\alpha - p^\beta\right) = 2\sigma_s + O\left(\frac{1}{R_s^2}\right) \qquad (4.9)$$

We now have a formula for the surface tension of a spherical surface:

$$\sigma_s = \frac{kT}{2}\int_{-\infty}^{\infty} dz_1\, \rho'(z_1) \int d\underline{r}_2\, c(\underline{r}_1,\underline{r}_2)\left(x_{12}^2 + y_{12}^2\right) \times \rho'(r_2) + O\left(\frac{1}{R_s^2}\right) \qquad (4.10)$$

which, like the thermodynamic results in Chapter 2, has only the leading order asymptotic variation. This is exactly the expression which Henderson and Schofield (1982) obtain from their own formalism for the free energy of inhomogeneous systems. In their derivation the arbitrariness in choosing the equimolar surface is replaced by one which arises from having to choose a volume conserving external field; in this case the stepfunction interface can be handled exactly. Their work strongly suggests that (10) is exact up to terms of order R_s^{-1} .

CHAPTER 5 THE PENETRABLE-SPHERE MODEL - BULK PHASES AND THE MEAN-FIELD APPROXIMATION

In this chapter a molecular model of a liquid (Widom and Rowlinson, 1970) is introduced. This model is used in later chapters to obtain numerical results for the density profile and surface tension of both spherical and planar systems. In the form we shall use here, the model represents a one-component system, the phase diagram of which has a liquid-vapour coexistence region. The model gets its name from the form of its interaction potential which, as we shall see later, is determined by the fraction of the total volume occupied by a sphere drawn about each particle. The model has the unusual but useful property that it is completely isomorphous with a particular hard-sphere system which represents a symmetrical mixture of species a and b. It can equally well be described in terms of the variables of either the one- or the two-component systems. In what follows the phrase 'the model' will refer to the one-component system whether or not it is described in the variables of the equivalent two-component system. Where necessary this two-component system will be distinguished by reference to 'the isomorphous mixture'. In general the equations which describe the model are more concisely written in the variables of this latter system; in particular the symmetry of the model is much clearer. 'Transcription relations' express the properties of the one-component system in the variables of the isomorphous mixture. Rowlinson (1980) gives a complete set of these relations as well as an extensive review of the model and its variants.

The isomorphous mixture has an interaction potential which is the sum of pair potentials between the species a and b

defined by the equations

$$u_{aa}(r) = u_{bb}(r) = 0$$
$$u_{ba}(r) = u_{ab}(r) = \begin{cases} \infty & (r \leqslant l) \\ 0 & (r > l) \end{cases} \qquad (5.1)$$

The system described by (1) is a simple mixture of fluids which at low density behaves as a mixture of perfect gases. At higher densities the repulsive part of the potential drives the system into two symmetrical phases, one rich in a, the other rich in b. The hard sphere interaction potential in (1) means that the configurational properties of the fluid do not depend on temperature - the Boltzmann factor has the value zero or unity always. For this reason the mixture can have the same number of degrees of freedom (in the thermodynamic sense) and can be 'isomorphous' with the one-component version.

The properties of the one-component system can be obtained by 'transcription' of the partition function of the system described in (1). If the grand canonical partition function of the mixture is written down and an integration performed over the positions of the b-molecules, the result can be rearranged into the form of a partition function for a single-component system. The transcribed partition function then defines the properties of the penetrable-sphere model: in particular the interaction potential becomes

$$\frac{U(\underline{N_a})}{kT} = \Big(W(\underline{r}_{a1}, \underline{r}_{a2}, \ldots \underline{r}_{aN_a}) - N_a v_0\Big)\frac{\lambda_b}{v_0} \qquad (5.2)$$

W is a term which is equal to the volume filled by spheres now of radius l centred on the positions of the a-molecules, $r_{a1}, \ldots$. From (1) these spheres are freely interpenetrating, hence the name of the model. Because of the nature of the transcription process, (1) and (2) are equivalent in that they give rise to identical configurations of α-molecules. The form of (2) identifies λ_b as an effective temperature; defining ε by

$$\varepsilon = \lambda_b kT \qquad (5.3)$$

an energy characterising the interaction potential is introduced. This may be used together with the characteristic length, ℓ , and volume, $v_0 = \frac{4\pi}{3}\ell^3$, to non-dimensionalise all thermodynamic quantities, such as density ($\rho = Nv_0/V$) and energy density ($\phi = Uv_0/V\varepsilon$). (A list of penetrable-sphere variables is given in the Table of Symbols). For those familiar with the use of reduced variables to describe the Lennard-Jones fluid, it might be worth noting that the different choice for the characteristic volume results in the appearance of extra features of ($4\pi/3$) in some later equations.

Rowlinson (1980) gives a complete list of transcription relations. Among the most important are the following:

$$N = N_\alpha \qquad (\rho = \rho_\alpha) \qquad (5.4a)$$

$$\theta \equiv \varepsilon/kT = \lambda_b \qquad (5.4b)$$

$$\lambda = \lambda_\alpha \exp(-\lambda_b) \qquad (5.4c)$$

$$\pi^{(1)}(\lambda, \theta) = \pi^{(2)}(\lambda_a, \lambda_b) - \lambda_b \qquad (5.4d)$$

Equation (4a) is very convenient as it means that the density profile is simply the density profile of component a in the isomorphous mixture. Equation (4b) is simply a definition of the temperature scale which, from (3), is identical to the activity λ_b. If temperature, and hence λ_b, is constant, then constancy of λ (through a liquid-vapour interface) is equivalent to that of λ_a in the isomorphous mixture - this is used later in setting up the equations for the density profile. Finally, the pressure-temperature ratio π $(= pv_0/kT)$ is introduced in (4d) (the superscripts indicate one- or two-component systems). The quantity $\pi^\alpha - \pi^\beta$, which is proportional to $p^\alpha - p^\beta$, clearly has the same value in both systems.

The interaction potential (2) depends only on the configuration of the a-molecules, equivalently the configuration of penetrable-sphere molecules. For this reason the b-molecules are sometimes referred to as ghosts: it is their presence in the isomorphous mixture (1) which gives rise to the forces between a-molecules implied by (2). Unfortunately, the integral (2) cannot be evaluated, although much progress can be made without it particularly in elucidating the phase behaviour of bulk fluids for which the reader is referred to Rowlinson (1980). For interfacial systems it becomes necessary to introduce an approximation at an early stage: this is the mean-field approximation which we now outline.

For a very interesting account of the application of mean-field theories to fluids in general see Chapter 5 of Rowlinson and Widom (1982). In applications to the penetrable-sphere model results of an unusually high consistency are possible. We can only briefly list some of the properties of the model in a mean-field approximation (mfa).

(a) It becomes exact at high temperatures: $\varepsilon/kT\ (=\lambda_b) \to 0$ (this is a general property of the mfa).

(b) It becomes exact for very high and very low densities, thus it treats the two-phase zero-temperature system exactly. This is the reason for the importance of the zero-temperature result of Chapter 10.

(c) In it the compressibility equation and pressure equation lead to the same equation of state. Also the Triezenberg -Zwanzig and Kirkwood-Buff equations for the surface tension give identical values.

(d) The virial series for the pressure in the isomorphous mixture is truncated thus:

$$\pi^{(2)} = \rho_a + \rho_b + \rho_a \rho_b \tag{5.5}$$

(e) The mfa becomes exact when the model is generalised to a space of infinite dimensionality. This is the origin of (c). In a system of infinite dimensionality each molecule has infinitely many nearest neighbours; in this respect it is like a system of very high density - cf. (b).

Nearly all the applications of the model in later chapters are in conjunction with the mfa.

The most convenient way to implement the approximation is to use (a). This effectively sets the Boltzmann factor to unity, so that canonical averages may be replaced by unweighted or 'random' averages. Simple geometric arguments can be used to obtain the fractional volume covered by a random configuration of penetrable-spheres in a homogeneous system. The equation for the configurational energy then becomes

$$\phi \equiv \frac{\langle u \rangle v_0}{V \varepsilon} = 1 - \rho - e^{-\rho} \qquad (5.6)$$

By very similar arguments the energy density and other thermodynamic properties in a system with an interface can be obtained. The only major qualitative failing of the mfa is near the critical point where the effect of density fluctuations, which it neglects, becomes important. Even here these effects are dimensionality dependent - hence the validity of (e) at all temperatures.

We finish this chapter by quoting an extremely useful result for the dcf of the model in an mfa. It was first obtained by Guerrero, Rowlinson and Sawford (1974) for a bulk phase, although it is in fact valid in a system with an interface of arbitrary geometry (Leng, Rowlinson and Thompson, 1977). The formula is

$$c(\underline{r}_1, \underline{r}_2) = \frac{1}{v_0} \int_{\tilde{v}} d\underline{r}_3 \, \rho_b(\underline{r}_3) \qquad (5.7)$$

v_0 is $(4\pi/3)\ell^3$ or $(4\pi/3)$ if dimensionless units are used for $\underline{r}_3$; $\tilde{v}$ is the volume common to two intersecting spheres centred on $\underline{r}_1$ and $\underline{r}_2$.

CHAPTER 6 THE PLANAR LIQUID-VAPOUR INTERFACE OF THE MODEL FLUID

The theory of the planar interface of the penetrable-sphere model is an essential starting point for the development of the theory of the spherical interface. Many of the methods used on the planar interface by Leng, Rowlinson and Thompson (1976, 1977) have direct parallels in the spherical case. Intuition and the thermodynamics of Chapter 2 lead us to expect that the density profile and the suface tension will be similar in planar and drop systems. Indeed the properties of a planar system in the absence of an external field may conveniently be defined as large radius limits of those of a spherical system (Yang, Fleming and Gibbs, 1976). Therefore, in this chapter a fairly detailed account of the planar theory, particularly the results of Leng, Rowlinson and Thompson (1976,1977), is presented.

The starting point for the generalisation of the theory of homogeneous phases is to choose a definition for the energy density at a height z in a system with a liquid-vapour interface in the x-y direction. Leng, Rowlinson and Thompson (1976) chose to consider an overlap area in place of the overlap volume used in the last chapter. This is the area covered on a plane at height z by penetrable-spheres at all neighbouring heights $z+u$. The mean-field approximation may then be introduced by assuming a random configuration of molecules within any plane. The original arguments of Leng, Rowlinson and Thompson (1976) for the analogue of (5.6) involve taking an infinite area limit and thus cannot be generalised to a spherical interface. The following derivation, which leads to the same result, can however.

Consider a plane of constant density (ie. parallel to the interface) at height z . The fractional area of this plane covered will be numerically equal to the probability of finding a point in the plane covered by a molecule. The constribution from molecules with centres in a slice of thickness δu around the height $z+u$ will be

$$p(z+u,\delta u) = \frac{N(z+u,\delta u)\,\mathcal{A}_c}{\mathcal{A}} \tag{6.1}$$

where $N(z+u,\delta u)$ is the number of centres in the slice, $\mathcal{A}_c$ is the area on the plane at z covered by <u>one</u> of them and $\mathcal{A}$ is the total area of the interface. (Overlaps, which make (1) disappear, may be eliminated in the limit $\delta u \to 0$). The quantity N will be determined by the density profile:

$$N(z+u,\delta u) = \frac{\rho(z+u)\,\mathcal{A}\,\delta u}{v_0} \tag{6.2}$$

In order to assess the contribution of particles at <u>all</u> heights we use a standard technique and work out the complementary probability, $p'(z)$, that a point on the plane at height z is not being covered. This will be a product of the corresponding single height probabilities - each given by $1-p(z+u,\delta u)$. This is most conveniently obtained by first taking logarithms

$$\ln(1-p(z+u,\delta u)) = -p(z+u,\delta u) + O(\delta u^2) \tag{6.3}$$

where again the equality becomes exact as $\delta u \to 0$. The logarithm of $p'(z)$ may be obtained by summing the logarithm in (3). This sum , in the limit $\delta u \to 0$ becomes an integral when (2) is used

$$\ln p'(z) \equiv -\sigma^*(z) = \int du\, \rho(z+u) \frac{d_c}{v_0} \qquad (6.4)$$

Leng, Rowlinson and Thompson (1976) introduced $\sigma^*(z)$ defined by (4) in terms of which the energy density $\phi(z)$ can be simply expressed by the generalisation of (5.2):

$$\phi(z) = 1 - \exp(-\sigma^*(z)) - \rho \qquad (6.5)$$

From this equation a number of other quantities which vary through the interface may be obtained in terms of $\sigma^*(z)$. For example, the transcription relation for ρ_b is (Rowlinson, 1980)

$$\rho_b(\underline{r}) = \lambda_b(1 - \rho(\underline{r}) - \phi(\underline{r})) \qquad (6.6)$$

from which, in a planar system, ϕ may be eliminated to leave

$$\rho_b(z) = \lambda_b \exp(-\sigma^*(z)) \qquad (6.7)$$

The interaction potential (5.1) ensures a complete symmetry between species a and b. For a planar interface this leads to a relation between the a and b profiles:

$$\rho_b(z) = \rho_a(-z) \qquad (6.8)$$

in which the origin of z is the point of symmetry, see Figure 4. In the isomorphous model σ^* will have analogues σ_a^* and σ_b^*. They are obtained by replacing ρ in (4) by ρ_a

and ρ_b respectively. The quantity σ_a will therefore satisfy

$$\rho_b(z) = \lambda_b \exp\left(-\sigma_a^*(z)\right) \tag{6.9}$$

The $a-b$ symmetry of the isomorphous mixture leads to the additional equation,

$$\rho_a(z) = \lambda_a \exp\left(-\sigma_b^*(z)\right) \tag{6.10}$$

Equations (4), (8) and (9) may now be combined to yield a closed expression for the density profile

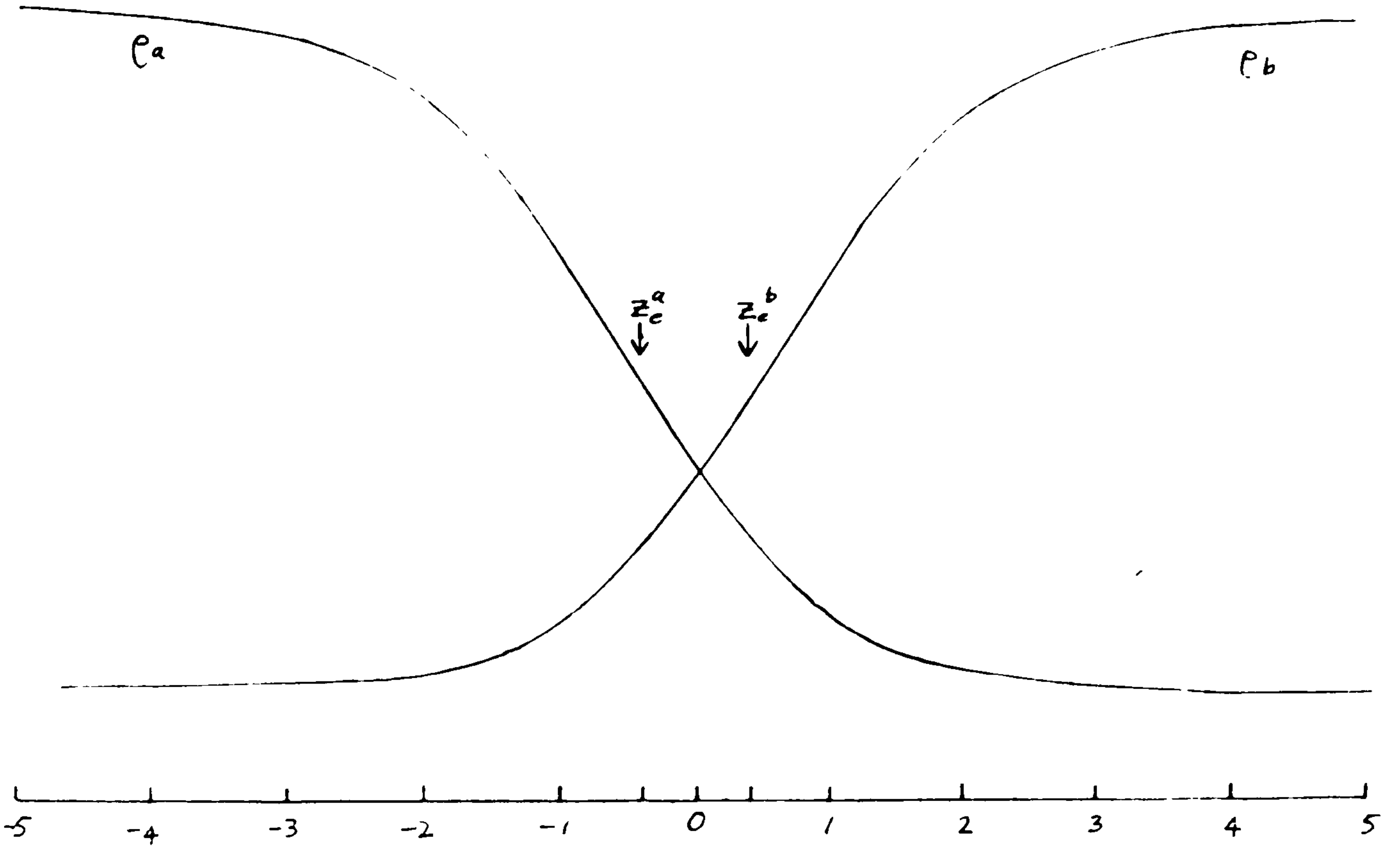
$$\ln\left[\frac{\rho_a(-z)}{\lambda_b}\right] = \frac{-3}{4}\int_{-1}^{1} du\, \rho_a(z+u)\left(1-u^2\right) \tag{6.11}$$

In this equation the explicit form for the geometrical factor $\mathscr{A}_c$ has been used:

$$\mathscr{A}_c = \begin{cases} \pi\left(1-u^2\right) & (|u| \leq 1) \\ 0 & (|u| > 1) \end{cases} \tag{6.12}$$

Leng, Rowlinson and Thompson (1976) were able to solve (11) numerically by successive substitution. Solutions are a one parameter (λ_b) family of curves of the general form sketched in Figure 4. The limiting values, at large $|z|$, of these curves are the bulk phase densities ρ^α and ρ^β which are known from the mean-field equation of state. This is used to set up an accurate form for the initial approximation required for the numerical method. A number of the features of this method are used in the calculations described later in this work, in

Figure 4. Symmetry in the planar system.



This figure shows two typical planar profiles having the symmetry expressed by (6.8). The origin of the abscissa is the centre of symmetry. (The scale corresponds roughly to a temperature of $0{\cdot}86T_c$.)

The equimolar surfaces z_e^a and z_e^b are also shown: these are discussed in Chapter 11.

Chapters 8 and 9.

Widom's potential-distribution theorem (Widom, 1963) can be used, as Leng, Rowlinson and Thompson (1976) showed, to define what is meant by the chemical potential of the model in the surface region. They were then able to show that it is constant at all points in the planar interface, as we should expect. This result is reversed later where the equation giving the spherical density profile is derived by constraining the chemical potential, given in terms of the density profile, to be constant.

Leng, Rowlinson and Thompson (1977) also obtained the equation (11) (in a different form) from a general integro-differential equation for the density.profile (cf. the remarks at the end of Chapter 3). An equivalent result can be shown for the equation for the spherical density profile; both methods rely on the use of (5.7) for the direct correlation function.

CHAPTER 7 PRELIMINARY SURVEY OF THE SPHERICAL SURFACE OF THE MODEL

In a system of C components with planar interfaces between the P phases there are exactly $C+2$ 'fields' (Griffiths and Wheeler, 1970) ($p, T, \mu_1 \ldots \mu_C$) which are independent but have the same value in each phase. In each of the P phases there is exactly one relation between these quantities (the Gibbs-Duhem equation for bulk phases). Therefore, the number of variables which characterise the system, F, is

$$F = C+2-P \tag{7.1}$$

This is the famous phase rule of Gibbs. In the previous chapter it was mentioned that the one-component two-phase system under discussion was characterised by the single temperature parameter, λ_b. This follows from (1) when we let $C=1$ and $P=2$. It might be noted that the isomorphous mixture is only a pseudo-two-component system because, unlike the one-component version it lacks a parameter corresponding to temperature - it is for this reason that the two versions can have isomorphous phase behaviour.

In a system with a curved interface there is no longer a unique pressure which characterises each of the bulk phases. To specify a system with a single radius of curvature it is necessary to specify the two bulk pressures, p^α and p^β, which appear in Laplace's equation (2.2). For a one-component spherical system we have, therefore, two degrees of freedom and we must expect any equation for the density profile to have two, not one, parameters that characterise the solutions. General modifications to the phase rule in the presence of curved surfaces are considered by Defay, Prigogine, Bellemans and Everett (1966).

For the above reasons the mean-field equation of state of the model in the two-phase region has to be modified in the presence of a curved surface. Equations determining the bulk phase densities, in the isomorphous mixture ρ_a^α , ρ_a^β , ρ_b^α and ρ_b^β , may be obtained by explicitly equating chemical potentials in the <u>homogeneous</u> phases α and β :

$$\lambda_a = \rho_a^\alpha \exp(\rho_b^\alpha) \tag{7.2}$$

$$\rho_a^\alpha \exp(\rho_b^\alpha) = \rho_a^\beta \exp(\rho_b^\beta) \tag{7.3}$$

$$\lambda_b = \rho_b^\alpha \exp(\rho_a^\alpha) \tag{7.4}$$

$$= \rho_b^\beta \exp(\rho_a^\beta) \tag{7.5}$$

and by using (5.4d) to express the pressure difference, $\Delta\pi$ between the two homogeneous phases α and β :

$$\pi^\alpha - \pi^\beta \equiv \Delta\pi = \rho_a^\alpha + \rho_b^\alpha + \rho_a^\alpha\rho_b^\alpha - (\rho_a^\beta + \rho_b^\beta + \rho_a^\beta\rho_b^\beta) \tag{7.6}$$

The four independent equations (3) to (6) then determine the bulk phase densities for given values of λ_b and $\Delta\pi$. The chemical potential, λ_a , may be obtained using (2). The quantity λ_b determines the temperature in the one-component version of the model by (5.4b) and $\Delta\pi$ is related to the size of the spherical system by the Laplace equation (2.2), written in reduced units:

$$\Delta\pi = \frac{2\sigma_s \lambda_b}{R_s} \tag{7.7}$$

The equations (2) to (6) are a set of (transcendental) algebraic equations. They can be solved by a generalised Newton-Raphson method (Wait, 1979) and a program to do this is listed in the Program Appendix. This algorithm is very robust and converges very rapidly for these equations. The accuracy with which this computation is carried out is limited only by machine precision amd thus introduces negligible errors into later calculations.

The qualitative conclusions about the phase behaviour of spherical systems yielded by the above analysis are exactly those which can be arrived at by using the Kelvin equation (Defay, Prigogine and Bellemans, 1966). In terms of the above notation, the chemical potential λ_a is increased from its value in a planar system at the same temperature (for which symmetry requires that $\lambda_a = \lambda_b$). Consequently the vapour in equilibrium with a drop of liquid is at a higher pressure than the vapour coexisting with a planar surface (or indeed any surface of lower curvature). For this reason a spherical system is never thermodynamically stable in the presence of a planar one. In isolation, however, a spherical system is indefinitely stable and has the geometry which minimises its superficial free energy.

Having determined the bulk phase densities in our system we may now turn to the profile itself. The method of Leng, Rowlinson and Thompson (1976), which depends on the use of the symmetry condition (6.8), can no longer be used. Their expressions for the chemical potentials in the isomorphous mixture, (6.9) and (6.10), are, however, very useful. These chemical potentials can be explicitly proved constant throughout the interface when the density profile satisfies (6.11). This is not suprising because they can be deduced from the potential-distribution theorem (Widom, 1963) which by its nature ensures constancy of chemical potential in an inhomogeneous system even in a canonical ensemble (Rowlinson and Widom, 1982, Chapter 4). For the spherical system we may start with the analogues of (6.9) and (6.10) for the chemical potential. Constancy of chemical potential, which may safely be assumed, will then lead to two equations which will be satisfied simultaneously by the two density profiles, $\rho_a(r)$ and $\rho_b(r)$.

The two equations will be

$$\lambda_a = \rho_a(r) \exp\left(-\sigma_b^*(r)\right) \tag{7.8}$$

$$\lambda_b = \rho_b(r) \exp\left(-\sigma_a^*(r)\right) \tag{7.9}$$

where σ_a^* and σ_b^* are as yet undetermined functionals of $\rho_a(r)$ and $\rho_b(r)$. We leave the generalisation of the arguments of Chapter 6 for these until the next chapter. Since (8) and (9) must be valid even in the bulk phases, λ_a and λ_b will have the values deduced from equations (2) to (6). This condition also ensures that σ_a^* and σ_b^* have the following limiting values, where the density is constant,

$$\operatorname*{lt}_{r\to R^{\alpha}} \sigma_a^*(r) = \rho_a^{\alpha} \quad ; \quad \operatorname*{lt}_{r\to R^{\beta}} \sigma_a^*(r) = \rho_a^{*} \qquad (7.10)$$

and similarly for σ_b^* . (As before, R^α and R^β are simply positions well inside the bulk phases). The other limiting behaviour required of σ_a^* and σ_b^* is that these functionals should become identical to their planar counterparts when the postiion of the equimolar surface, R_e , becomes large.

In the next chapter we obtain σ_a^* and σ_b^* explicitly and solve the resulting equations, (8) and (9), for the spherical profile.

CHAPTER 8 THE EQUATION FOR THE DENSITY PROFILE AND ITS NUMERICAL SOLUTION

The derivation of the equations for $\rho_a(r)$ and $\rho_b(r)$, started in the previous chapter, is completed in this one. They are a coupled pair of non-linear integral equations whose solution proves to be far from straightforward. A solution can, however, be obtained by combining physical reasoning with numerical analysis. This solution uses an unusual optimization algorithm which is reproduced in the Appendix.

To generalise the derivation of the key-quantity σ^* of Chapter 6, consider a spherical shell (rather than a planar slice) of thickness δu at a height $(r+u)$ from the drop-centre. The number of penetrable-sphere-molecule centres in this shell, for small δu, will be

$$N(r+u, \delta u) = \frac{\rho(r+u)}{v_0} \, 4\pi \, (r+u) \, \delta u \tag{8.1}$$

The probability that a point on the Gibbs surface at r is covered by these molecules is

$$p(r+u, \delta u) = \frac{N(r+u, \delta u) \, \mathcal{A}_c(r, u)}{4\pi r^2} \tag{8.2}$$

where (cf. (6.1)) $\mathcal{A}$ is the area covered by <u>one</u> molecule. As in the planar case, the complementary probability may be expanded to first order in δu

$$\begin{aligned} \ln(1 - p(r+u, \delta u)) &= -p(r+u, \delta u) + \mathcal{O}(\delta u^2) \\ &= \frac{\rho(r+u)}{v_0} \left(1 + \frac{u}{r}\right)^2 \mathcal{A}_c(r, u) \, \delta u \end{aligned} \tag{8.3}$$

The quantity we require, $\sigma^*(r)$, is the negative logarithm of this (complementary) probability, summed over all shells. In the limit $\delta u \to 0$ this may be written:

$$-\sigma^*(r) = -\frac{1}{v_0}\int du\, \rho(r+u)\left(1+\frac{u}{r}\right)^2 \mathcal{A}_c(r,u) \tag{8.5}$$

The function $\mathcal{A}_c$ is more complicated than its planar analogue in that it depends on r as well as u. The most important case occurs for Gibbs surfaces of radii larger than that of a single penetrable sphere. By simple geometry

$$\mathcal{A}_c(r,u) = \begin{cases} \pi(1-u^2)/(1+u/r) & (|u| \leq 1) \\ 0 & (|u| > 1) \end{cases} \tag{8.6}$$

The more unusual case, for Gibbs surfaces of less than one molecular radius is

$$\begin{aligned} \mathcal{A}_c(r,u) &= 4\pi r^2 && (-r \leq u \leq 1-2r) \\ &\quad \pi(1-u^2)/(1+u/r) && (1-2r \leq u \leq 1) \\ &\quad 0 && (-r > u > 1) \end{aligned} \tag{8.7}$$

Both (6) and (7) may be combined with (5) to give

$$\sigma^*(r) = \begin{cases} \frac{3}{4}\int_{-1}^{1} du\, \rho(r+u)\left(1+\frac{u}{r}\right)(1-u^2) & (r \geq 1) \\ 3\int_{-r}^{1-2r} du\, \rho(r+u)(r+u)^2 + & (r<1) \\ \quad + \frac{3}{4}\int_{1-2r}^{1} du\, \rho(r+u)\left(1+\frac{u}{r}\right)(1-u^2) & \end{cases} \tag{8.8}$$

This equation defines $\sigma_a^*(r)$ when ρ is replaced by ρ_a and $\sigma_b^*(r)$ when ρ is replaced by ρ_b.

It can be verified by direct substitution into (8) that has the property anticipated in (7.10) that where ρ is a constant we have

$$\sigma^*(r) = \rho \qquad (\rho \text{ const.}) \tag{8.9}$$

In this work we are concerned only with drops which can be described by the thermodynamic analysis of Chapter 2. For such drops it is necessary to have a region in the interior phase which is sensibly homogeneous. Therefore, even for values of R^{τ} in (7.10) less than unity, equation (9) enables the use of the more complicated form of σ^* for $r < 1$ to be dispensed with.

The simpler equations with which we shall deal from now on are then,

$$\begin{aligned}\rho_a(r) &= \lambda_a \exp(\sigma_b^*[\rho_b](r)) \\ &= \lambda_a \exp\left\{\frac{-3}{4}\int_{-1}^{1} du\, \rho_b(r+u)\left(1+\frac{u}{r}\right)(1-u^2)\right\}\end{aligned} \tag{8.10}$$

$$\begin{aligned}\rho_b(r) &= \lambda_b \exp(\sigma_a[\rho_a](r)) \\ &= \lambda_b \exp\left\{\frac{-3}{4}\int_{-1}^{1} du\, \rho_a(r+u)\left(1+\frac{u}{r}\right)(1-u^2)\right\}\end{aligned} \tag{8.11}$$

(The notation $\sigma_b^*[\rho_b](r)$ indicates that σ_b^* is a functional of ρ_b, and simultaneously a function of r).

It would be possible to eliminate the density profile of the 'ghost' component, ρ_b, between these equations, though at a considerable cost in added complexity. Also, the symmetry of the isomorphous mixture means that the ρ_b profile, which may be obtained from the separate equations, is, in fact, that of a 'drop' of vapour in equilibrium with its own liquid when a is the component with greater abundance in the interior phase. Such a 'bubble' profile is shown later in Figure 5.

There are a limited number of approaches to (10) and (11) which will be capable of yielding the global numerical solution we require (see particularly Rall, 1969 and Delves and Walsh, 1973, Chapters 15 and 16; also Baker, 1977 and Golberg, 1980). The most widely applicable methods involve iteration or successive substitution, starting from a given initial approximation. Methods of this sort are particularly attractive because a knowledge of the physics which underlies the equation will greatly facilitate the choice of a good initial approximation, which will in turn determine the convergence properties of the solution. In this particular case we know both the detailed form of the profiles in the large drop (planar) limit (Chapter 6) and the asymptotic values of the densities (Chapter 7). One approach to the solution of (10) and (11) would be to 'linearise' them and then use a generalised Newton-Raphson iteration. However, this procedure would involve obtaining the solution of two complicated (but linear) coupled Volterra equations at each iteration without any guarantee of an improved region of convergence. For this reason, particularly as (10) and (11) are already in fixed point form (Delves and Walsh, 1973, Chapter 15), the general strategy adopted by Leng, Rowlinson and Thompson (1976) is followed, and a direct iteration is chosen.

The iterations produce a sequence of functions, $\rho^{(n)}$:

$$\rho_a^{(n)}(r) = \omega \lambda_a \exp(-\sigma_b^*[\rho_b^{(n-1)}](r)) + (1-\omega)\rho_a^{(n-1)}(r) \qquad (8.12)$$

$$\rho_b^{(n)}(r) = \omega\lambda_b \exp(-\sigma_a^*[\rho_a^{(n-1)}](r)) + (1-\omega)\rho_b^{(n-1)}(r) \quad (8.13)$$

Here ω is a relaxation parameter which is introduced to improve the rate of convergence. Under-relaxation ($\omega < 1$) is used, with the value of ω chosen on the basis of a small number of trials.

To start the iteration an initial approximation to the density profile, $\rho^{(0)}(r)$, must be chosen. The most important thing about $\rho^{(0)}(r)$ is that it has the correct bulk phase densities. The range over which the solution is obtained is chosen so that the variation of density at its ends is negligible. In practice this is achieved by incrementing an initial range until the solution does not change. The exact form of the initial approximation takes two forms: at low temperatures (large values of λ_b), the zero-temperature stepfunction limit and, at higher temperatures, a mean-field planar critical hyperbolic tangent profile have been used.

There is one respect in which the density profiles for a spherical surface differ essentially from those for a planar surface. In the latter case the origin of the co-ordinate normal to the interface is arbitrary, and the position of the interface itself, as defined by, eg. the equimolar surface, does not enter into the equations. Conversely, in the case of a spherical interface, the centre of the drop is fixed absolutely; density profile functions will only be solutions to (10) and (11) if their equimolar surfaces are positioned correctly with respect to the origin.

In Chapter 7 it was discussed how λ_b and $\Delta\pi$ could be chosen as the independent variables in (7.2) to (7.6). These equations not only determine λ_a and λ_b in (10) and (11), but also, through the Laplace equation (7.7), one measure of the size of the drop - the position of the surface of tension, R_s . This last result is only a formal one, however, because the surface tension, σ_s , which enters into the Laplace equation is not known. However, if the planar surface tension, σ_∞ , is used, a rough estimate, $R_s^{(0)}$, of the size of a drop can be obtained.

It is desirable to choose the size of a drop, for a given $\Delta\pi$ and λ_b , carefully and if possible relate it to $R_s^{(0)}$ which is at least correct to zeroth order. The initial profile, $\rho^{(0)}$, cannot be directly related to $R_s^{(0)}$, but it can be chosen to have a particular value of R_e . R_e and R_s are linked by (2.24). For this model a zero-temperature limit gives δ explicitly. With this limit an approximation to the position of the equimolar surface, $R_e^{(0)}$, can be obtained for all temperatures. Additionally, the planar profiles provide a guide for the separation of the equimolar surfaces of the two components of the isomorphous mixture. Combining all this information enables good initial approximations to the two profiles, $\rho_a^{(0)}$ and $\rho_b^{(0)}$ to be constructed.

Having chosen the iteration sequence, (12) and (13), and the initial approximations, we are left with the task of choosing a convergence criterion. When the sequence (7.8), (7.9) has converged the quantity $\rho_a^{(n)}(r)\exp(\sigma_b^*[\rho_b^{(n-1)}](r))$ will, from (7.8), be the chemical potential, , which we know to be constant in the physical system. Before convergence it will vary somewhat through the interface; we may define the quantity $\delta\lambda_a^{(n)}$ to be the extent of this departure from the bulk phase value, λ_a , by

$$\delta\lambda_a^{(n)} = \max_{r \in R^*} \left\{ \rho_a^{(n)}(r) \exp(\sigma_b^*[\rho_b^{(n-1)}](r)) - \lambda_a \right\} \tag{8.14}$$

where R^* is some set of points in the interface. When the sequence of iterations have fully converged both $\delta\lambda_a^{(n)}$ and the analogous quantity $\delta\lambda_b^{(n)}$ will have vanished. In practice iteration was stopped when the quantity $Q^{(n)}$, defined by

$$Q^{(n)} = \left|\delta\lambda_a^{(n)}\right| + \left|\delta\lambda_b^{(n)}\right| \tag{8.15}$$

dropped below a small predetermined value.

Unfortunately, the procedure described above does not converge according to this criterion. For a given value of the position of the equimolar surface of the starting profile, $R_e^{(0)}$ $Q^{(n)}$ initially approaches its converged value, but then goes through a minimum finally increasing with n . Thus $Q^{(n)}$ shows the behaviour expected of partial sums in an asymptotic series: we shall refer to this as asymptotic convergence. As $Q^{(n)}$ decreases the form of the density profiles improves - eg. a stepfunction starting profile is converted into a smooth profile of the sort expected from planar solutions. As $Q^{(n)}$ increases, after asymptotic convergence, the profile maintains its shape but starts to drift bodily. Clearly what is required is to displace the iterated profile, as near to asymptotic convergence as possible, not back to its starting point, but to a position at which $Q^{(n)}$ can be reduced to such an extent that the convergence criterion is satisfied. Each displacement amounts to restarting the iteration sequence with a starting profile based on the 'best' profile of the previous sequence. To choose displacements to minimise $Q^{(n)}$ systematically is a problem in optimization theory (see eg. Carnahan and Wilkes, 1973) which can be dealt with by none of the usual methods. A new algorithm which can cope, however, is given in the Appendix.

The above procedures for solving equations (10) and (11) were incorporated in the FORTRAN program DROPSOLVE, listed in the Program Appendix. All calculations were carried out on a Data General 'Eclipse' computer in double precision arithmetic. The calculations were carried out with the main aim of computing profiles for which $Q^{(n)}$ is about 10^{-6} or less.

To evaluate the integrals in (10) and (11) DROPSOLVE uses a repeated Simpson rule with steplength H, the profiles being held on a linear grid of this spacing. The whole problem is discretized with this single stepsize for efficiency considerations. The quadrature to obtain the equimolar surface position, R_e , is also done with a repeated Simpson rule using this stepsize. More details of this calculation are given in the Appendix.

A given drop is specified by the parameters λ_a and λ_b which appear in (10) and (11). These determine the size and temperature of a drop as described in Chapter 7, where they are related to the bulk phase densities. Of all the parameters which must be supplied to DROPSOLVE these clearly are the most important. Their acceptable range is in part restricted by physical considerations, though it is also partly determined by the accuracy expected of the calculation. Thus drops for which the interior density is varying significantly within a molecular radius of the drop centre cannot be calculated by DROPSOLVE because only the first part of (8), with $r>1$, is used. Thus in practice it is not possible to obtain profiles with R_e less than about 10 molecular radii using DROPSOLVE, though this is weakly dependent on temperature. The range of temperatures at which calculations were carried out is also restricted for purely computational reasons. At low temperatures the profiles become increasingly step-function-like, requiring a smaller and smaller stepsize for their solutions; thus, no solutions have been attempted below $\sim 0.1\ T_c$. It is unfortunate that the calculations may not be taken nearer the zero of temperature because it is only at that limit that an analytic surface tension can be obtained, as we show in Chapter 10.

The time taken for computation also puts an upper limit on dropsize. As the size of the drop becomes very large, equations (10) and (11) become increasingly like the equations for a planar profile, which as has been discussed, are invariant to the choice of equimolar surface. It is not suprising, therefore, that the algorithm to minimize $Q^{(n)}$, which effectively fixes the position of the equimolar surface for the drop, converges only slowly at large dropsize. DROPSOLVE can successfully produce profiles for drops of radii up to about 100 molecular radii; these are practically indistinguishable from planar profiles.

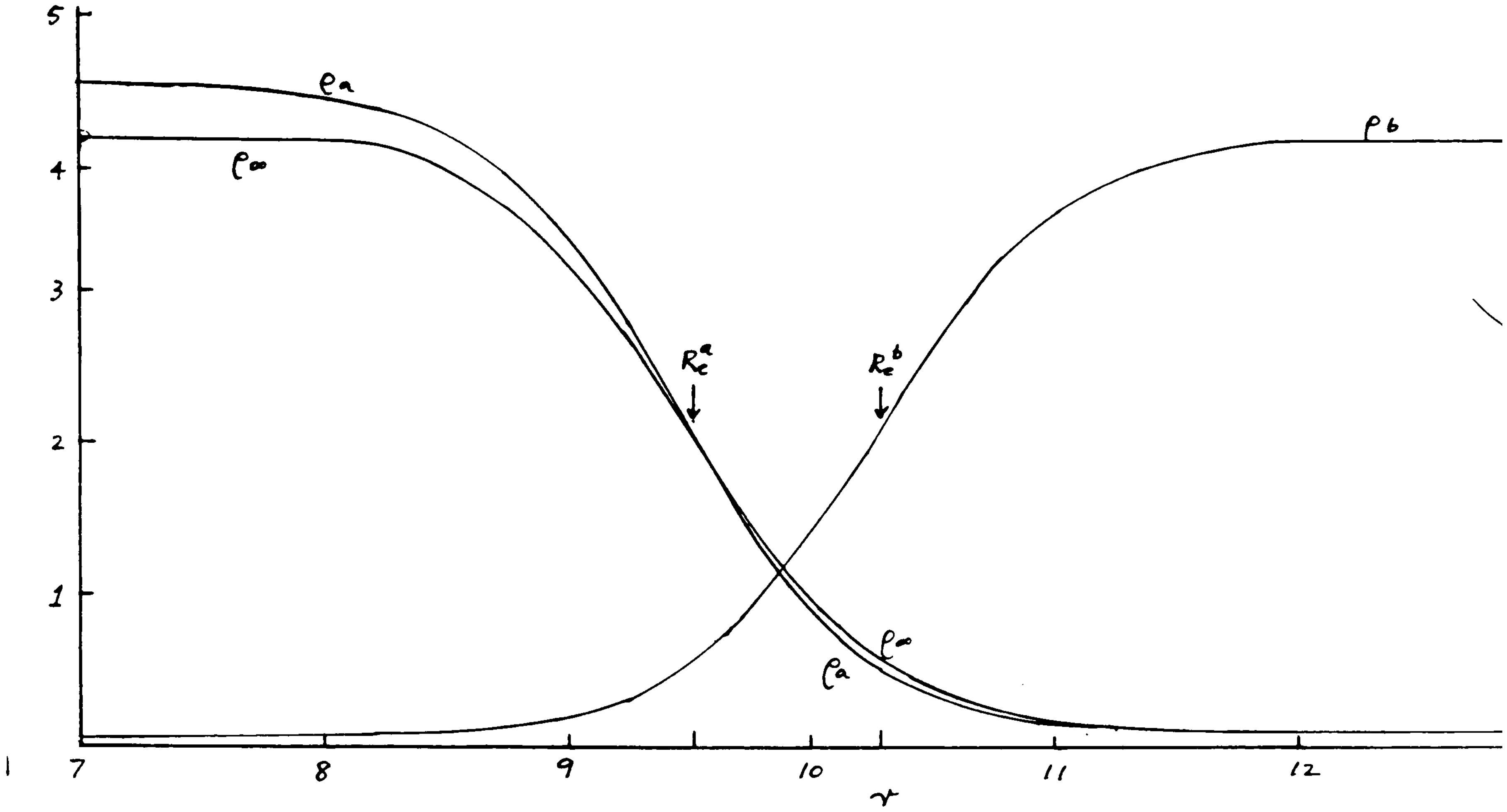
There are a number of other parameters which have to be supplied to DROPSOLVE. These include the stepsize H which controls the discretization error resulting from representing a continuum problem, like (10) and (11), on a grid of finite mesh size. This error is largely due to the truncation error in the numerical quadrature. The discretization also has a separate effect on the rather complicated iteration procedure. Thus, although $Q^{(n)}$

may be reduced practically without limit, and therefore the discretized version of the problem defined by (10) and (11) may be in principle solved exactly, this solution approaches the solution to the original problem only in the limit of zero H. A further minor effect of discretization is that the maximisation to obtain $Q^{(n)}$ (equation (14)) can now be done only over the set of grid points at which the densities are calculated (cf. Barrodale, 1973). Rather than analyse these errors separately we use the known result that they all vanish when H tends to zero. Then we assume that the error is comparable with the change in the solution when the steplength is halved and choose the steplength so that the combined discretization errors affect only the fifth significant figure. For a wide range of temperatures (dropsize is unimportant in this instance because it influences the gradients of the profile only slightly) a stepsize of one tenth of a reduced unit (penetrable-sphere radius) is adequate when using DROPSOLVE.

The only other important physical parameters which need to be supplied are the R^{κ} and R^{β} of (7.10). These determine the number of nodes in the grid and therefore have an important influence on the time taken by the calculation but are otherwise easily chosen.

Two sample profiles are shown in Figures 5 and 6. In Figure 5 the density profile of a bubble at the same temperature is shown; as explained above this is simply the density profile of the ghost component, $\rho_b(+)$. As can be seen from the diagrams the density profile is qualitatively very similar to that of a planar surface at the same temperature - both are smooth monotonic sigmoidal functions. The difference in the asymptotic values

Figure 5. Drop density profile



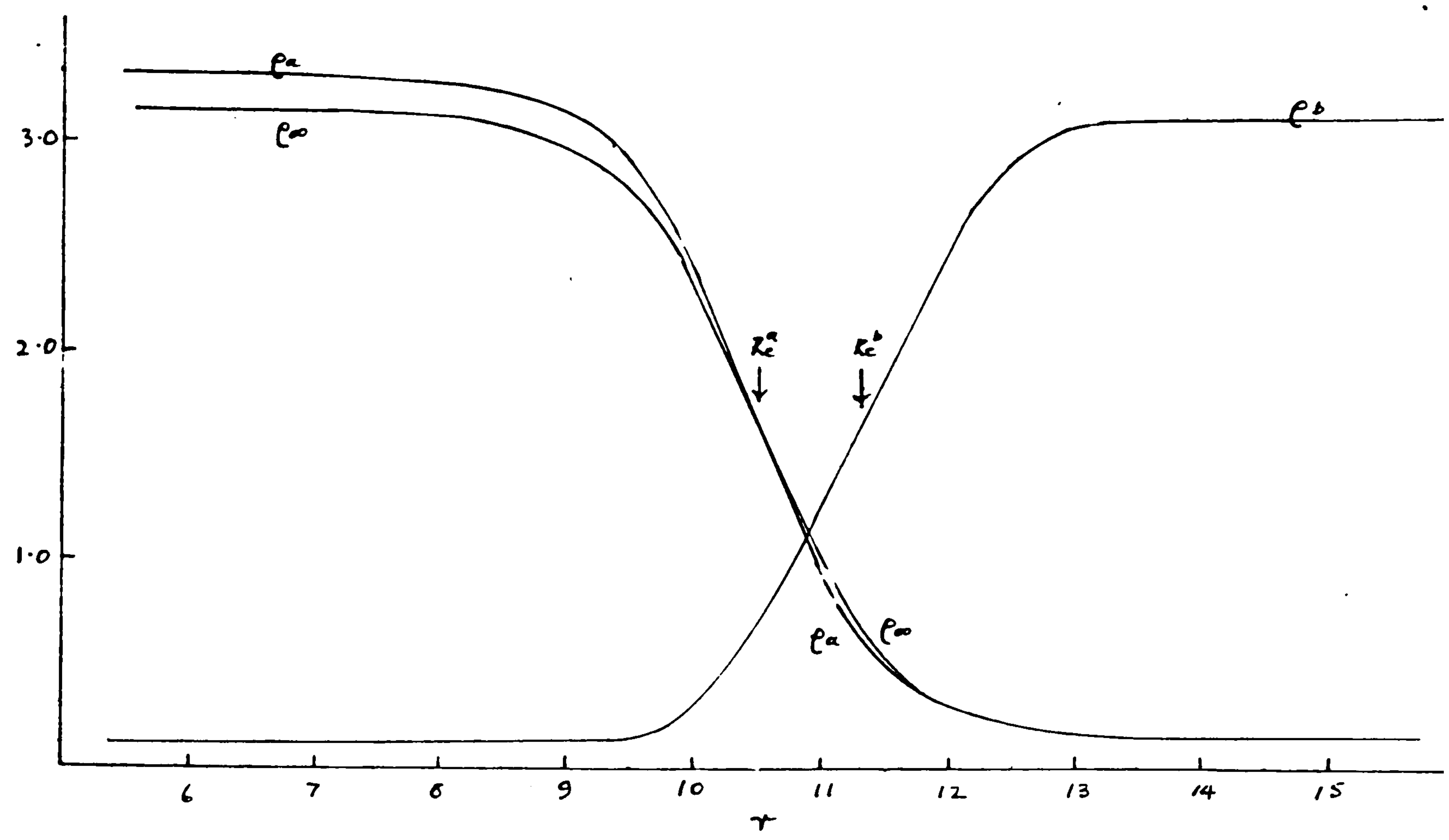
The curves shown are as follows:

ρ_a - the density profile of a drop at $T = 0.619\,T_c$, a solution of (8.10) and (8.11)

ρ_b - the density profile of component b of the isomorphous mixture. The a-b symmetry of the model means that if the usual transcription is reversed this profile corresponds to a bubble of vapour in equilibrium with its liquid.

ρ_∞ - the density profile of a planar interface at $0.619\,T_c$, with its equimolar surface aligned with that of ρ_a. Comparison of this with ρ_a shows the effect of curvature on the profile and the bulk phase densities.

Figure 6. Drop density profile



The curves are as those in Figure 5, at the higher temperature of 0.735 T_c.

away from the interface have been analysed in the previous chapter. It is only the remaining small difference in the behaviour of the profile in the vicinity of its maximum gradient which, as we shall see later, is crucial to obtaining correct values for the surface tension.

Now that the problem of finding the density profile has been solved we may turn to the problem of calculating the surface tension. The formula derived in Chapter 4 requires considerable manipulation before it can be used with the penetrable-sphere model. This is the topic of the next chapter. It is then used to obtain numerical results in Chapter 10.

CHAPTER 9 SURFACE TENSION OF MODEL FLUID DROPS

In Chapter 4 a general expression for the surface tension of a drop was derived. One aim of this work is to test this new expression using the penetrable-sphere model. The quantities in the expression (equation (4.10)) are already known, or can be calculated: the direct correlation function from (5.7) and the density profiles from the previous chapter. For numerical purposes, however, the expression is far from satisfactory - it is a four-fold integral over an integrand which depends on the direct correlation function, which itself is defined as a volume integral. Therefore, considerable analytic simplifications are necessary if progress is to be made. Before we attempt to make this simplification we consider a related problem, namely, the simplification of an integrodifferential equation for the profile. This is the rather general equation mentioned at the end of Chapter 3, which again involves the direct correlation function. It is further discussed for a planar profile in Chapters 11 and 12. At the end of this chapter an important analytic limiting form for the surface tension at zero-temperature is obtained. This has in fact already been used to gain an approximate idea of the relationship between the positions of the equimolar surface and the surface of tension, for use in setting up an initial approximation for the iterative procedure as explained in the previous chapter.

The integrodifferential equation for the profile (Lovett, Mou and Buff, 1976, Wertheim, 1976; see also Evans, 1979) which we use is, in reduced units

$$\underline{\nabla}_1 \ln \rho(\underline{r}_1) = \frac{3}{4\pi}\int d\underline{r}_2\, c(\underline{r}_1, \underline{r}_2)\, \underline{\nabla}_2\, \rho(\underline{r}_2) \qquad (9.1)$$

We will substitute into (1), specialized to a spherical geometry, the direct correlation function (5.7) expressed in the form

$$c(\underline{r}_1,\underline{r}_2) = \frac{3}{4\pi}\int d\underline{r}_3\, f(r_{13})\, f(r_{23})\, \rho_b(\underline{r}_3) \tag{9.2}$$

where $f(r)$ is defined by

$$f(r) = \begin{cases} -1 & (r \leq 1) \\ 0 & (r > 1) \end{cases} \tag{9.3}$$

and, as usual, $r_{12} \equiv |\underline{r}_2 - \underline{r}_1|$. Equation (1) is valid for a one-component system; although ρ_b has no direct physical significance in the one-component model it can always be related to physical variables of the one-component system by the transcription relation (6.6).

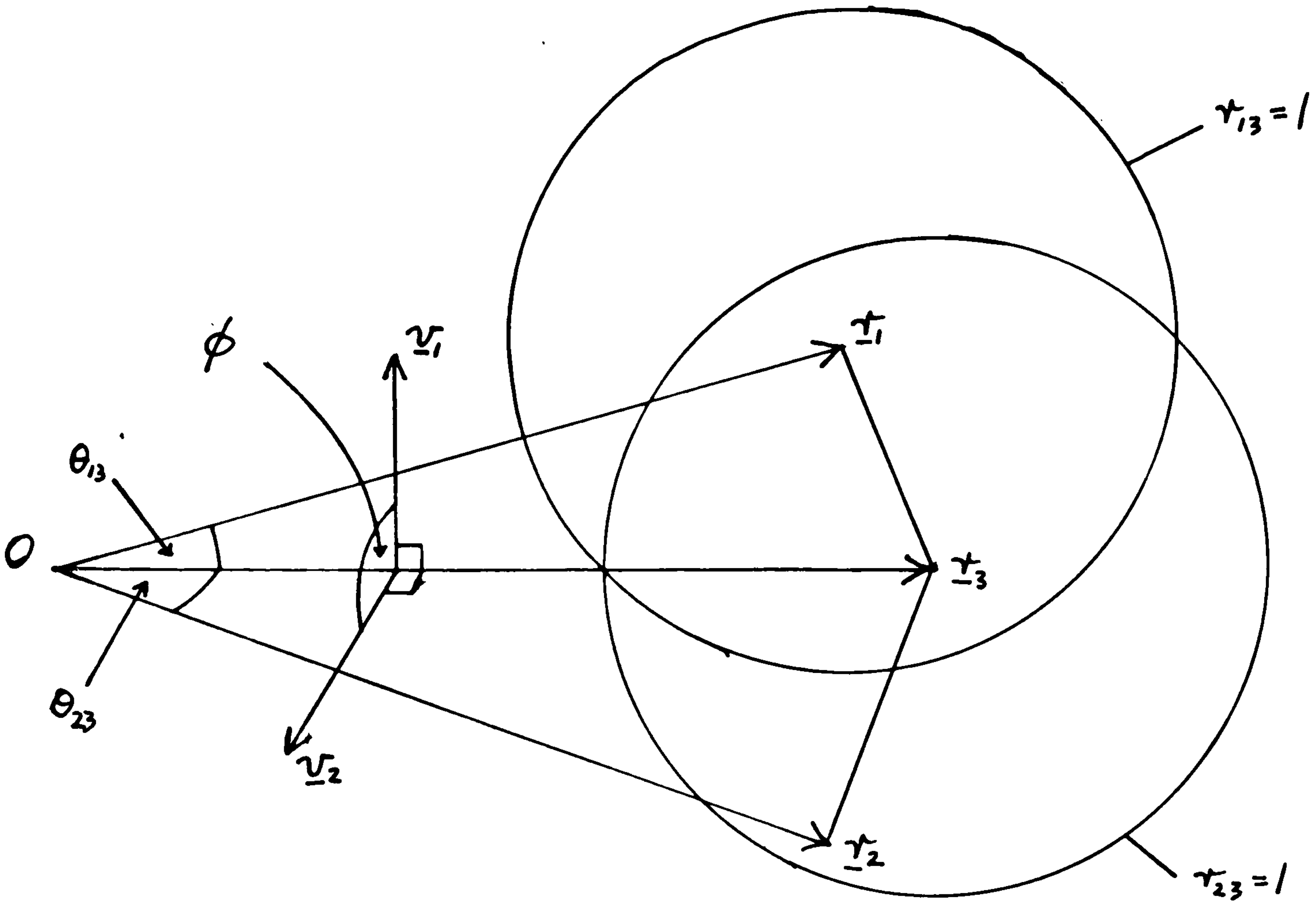
Considerable simplifications result if the symmetry of the system is taken into account. The integration over $\underline{r}_3$ is limited to the volume of overlap of the two spheres shown in Figure 7. Radial symmetry ensures that densities are functions only of a scalar distance from the centre of the drop as origin (see Figure 7). Taking the scalar product of both sides of (1) with a unit vector in the direction of $\underline{r}_1$, $\hat{\underline{r}}_1$, simplifies it to

$$\frac{d}{dr_1}\ln\rho(r_1) = \left(\frac{3}{4\pi}\right)^2 \int d\underline{r}_2 \int d\underline{r}_3\, f(r_{13})\, f(r_{23}) \times \\ \times\, \rho_b(r_3)\, \rho'(r_2)\, \hat{\underline{r}}_1 \cdot \hat{\underline{r}}_2 \tag{9.4}$$

If the integration over $d\underline{r}_2$ is taken inside the integral the result can be simplified using

$$\int d\underline{r}_2 \equiv \frac{1}{r_3}\int_0^\infty dr_2\, r_2 \int_{|r_3-r_2|}^{r_2+r_3} dr_{23}\, r_{23} \int_0^{2\pi} d\phi \tag{9.5}$$

Figure 7. Bipolar coordinate system.



The origin, 0, is the centre of the drop so that the densities ρ_a and ρ_b are functions of the magnitudes of $\underline{r}_1$, $\underline{r}_2$ and $\underline{r}_3$ only. The integration over $\underline{r}_2$ in (9.4) is carried out in terms of r_2, r_{23} and ϕ.

The vector $\underline{v}_1$ is in the plane containing $\underline{r}_1$ and $\underline{r}_2$, and $\underline{v}_2$ is in that containing r_2 and r_3; both are perpendicular to $\underline{r}_3$.

In the integration over $\underline{r}_2$ in (9.4) the factor $f(r_{13})$ confines r_2 to the sphere $r_{13}=1$, a section through which is shown. The subsequent integration over $\underline{r}_3$ is confined to the sphere $r_{13}=1$ - this is also shown.

In this equation ϕ is the angle between the vectors $\underline{v}_1$ and $\underline{v}_2$, which are both perpendicular to $\underline{r}_3$, as shown in Figure 7. These vectors can be expressed in terms of other vectors in the problem by the appropriate projection:

$$\underline{v}_1 = \hat{\underline{r}}_1 - \hat{\underline{r}}_3 \, (\hat{\underline{r}}_1 \cdot \hat{\underline{r}}_3) \qquad \underline{v}_2 = \hat{\underline{r}}_2 - \hat{\underline{r}}_3 \, (\hat{\underline{r}}_2 \cdot \hat{\underline{r}}_3) \tag{9.6}$$

Equation (6) can be used to obtain $\hat{\underline{r}}_1 \cdot \hat{\underline{r}}_2$ (in(4)) in terms of ϕ :

$$\hat{\underline{r}}_1 \cdot \hat{\underline{r}}_2 = \cos\theta_{23} \cos\theta_{13} + \sin\theta_{13} \sin\theta_{23} \cos\phi \tag{9.7}$$

(Now the dot products have been expressed in terms of the angles between the vectors). With this (4) becomes

$$\frac{d}{dr_1} \ln \rho_a(r_1) = \frac{18}{16\pi} \int d\underline{r}_3 \, \frac{f(r_{13})}{r_3} \rho_b(r_3) \cos\theta_{13} \times \times \int_{|r_3 - r_2|}^{1} dr_{23} \, r_{23} \cos\theta_{23} \tag{9.8}$$

the integral over ϕ has been evaluated and the limits on the two innermost integrals have been modified in accord with the range of non-zero $f(r_{23})$.

The innermost integral in (8) may be evaluated and the results simplified with the substitution $u = r_2 - r_3$. We now have

$$\frac{d}{dr_1} \ln \rho_a(r_1) = \frac{9}{64\pi} \int d\underline{r}_3 \, \rho_b(r_3) \, \frac{f(r_{13})}{r_3} \cos\theta_{13} \times \times \int_{-1}^{1} du \, (1-u^2)[(2r_3+u)^2 - 1] \rho'(r_3+u) \tag{9.9}$$

The new innermost integral may be shown from the definition (8.11) to be essentially $\frac{d}{dr_3} \sigma_a^*(r_3)$ (apart from a factor of $16 r_3^2/3$). If we differentiate one of the two equations for the density profile, (7.9), the equation

$$\rho_b'(r) = \rho_b(r)\,\sigma_a^{*\prime}(r) \tag{9.10}$$

is obtained. These results in (9) yield

$$\frac{d}{dr_1} \ln \rho_a(r_1) = \frac{16}{3}\,\frac{9}{64\pi} \int d\underline{r}_3\, \rho_b'(r_3)\, f(r_{13}) \cos\theta_{13} \tag{9.11}$$

The integral over $\underline{r}_3$ in this is now of exactly the same form as the integral over $\underline{r}_2$ in (4)! A repetition of the above steps then leaves

$$\frac{d}{dr} \ln \rho_a(r) = \frac{d}{dr}\,\sigma_b^*(r) \tag{9.12}$$

But this is the derivative of the equation (7.8) which is the complementary part of the equation for the density profile. Thus, (1) is equivalent to the derivative of the equation for the density profile which expresses the constancy of chemical potential. Evans (1979) gives a derivation of (1) which reveals it to be the gradient of the equation for thermodynamic equilibrium in terms of the chemical potential, putting the earlier derivation on an even more secure foundation.

The procedure for expressing the equation for the surface tension (4.10) in terms of the penetrable-sphere model variables follows the above procedure closely. In dimensionless variables (4.10) becomes

$$\sigma_s = \frac{1}{v_0} \cdot \frac{1}{4\lambda_b} \int_0^\infty dr_1\, \rho'(r_1) \int d\underline{r}_2\, c(\underline{r}_1, \underline{r}_2)\, \underline{r}_2^2 \sin\theta_{12}\, \rho'(r_2) \tag{9.13}$$

The direct correlation function (2) is introduced and the integration over $\underline{r}_2$ rewritten in terms of (5):

$$\sigma_s = \frac{1}{v_0^2}\frac{1}{4\lambda_b}\int_0^\infty dr_1\, \rho'(r_1) \int d\underline{r}_3\, f(r_{13})\, \frac{\rho_b(r_3)}{r_3} \times$$

$$\times \int_{r_3-1}^{r_3+1} dr_2\, r_2^3\, \rho'(r_2) \int_{|r_2-r_3|}^{1} dr_{23}\, r_{23} \int_0^{2\pi} d\phi\, \sin^2\theta_{12} \tag{9.14}$$

The innermost integral may be evaluated and the result simplified with the substitution $u = r_2 - r_3$ as before; when the function F defined by

$$F(r,u) = 1 - \frac{(1-u^2)}{2r(r+u)} \tag{9.15}$$

is introduced we have

$$\sigma_s = \frac{1}{v_0^2}\frac{\pi}{8\lambda_b}\int_0^\infty dr_1\, \rho'(r_1)\int d\underline{r}_3\, f(r_{13})\, \frac{\rho_b(r_3)}{r_3}\int_{-1}^{1} du\,(1-u^2)(r_3+u)^3 \times$$

$$\times\, \rho'(r_3+u)\left\{1+\cos^3\theta_{13}+\left(\tfrac{1}{3}-\cos^2\theta_{13}\right)\left(1+F(r_3,u)+F^2(r_3,u)\right)\right\} \tag{9.16}$$

Further simplifications follow the introduction of the analogue of (5) for the integration over $\underline{r}_3$:

$$\sigma_s = \frac{1}{v_0^2}\frac{\pi}{4\lambda_b}\int_0^\infty dr_1\, \frac{\rho'(r_1)}{r_1}\int_{r_1-r_3}^{r_1+r_3} dr_3\, \rho_b(r_3)\int_{-1}^{1} du\,(1-u^2)(r_3+u)^3 \times$$

$$\times\, \rho'(r_3+u)\left\{1+\cos^2\theta_{13}+\left(\tfrac{1}{3}-\cos^2\theta_{13}\right)\left(1+F+F^2\right)\right. \tag{9.17}$$

The presence of density derivatives in the integrand ensures that there will be a non-zero contribution to the integral only in the region of the interface itself. Therefore, since the original formula for the surface tension, (4.10) is correct only up to $\mathcal{O}(R_e^{-1})$ we may expand the integrand in powers of r^{-1} , neglecting terms of order r_1^{-2} . This yields (with $\nu = r_3 - r_1$)

$$\sigma_s = \frac{1}{v_0^2}\frac{\pi^2}{8\lambda_b}\int_0^\infty dr\,\rho'(r)\int_{-1}^{1} du\int_{-1}^{1} dv\,(1-u^2)(1-v^2)\left(1+\frac{3u+3v}{r}\right)\times$$
$$\times\,\rho'(r+u+v)\,\rho_b(r+u)\left[(1-u^2)\left(1-\frac{u+v}{r}\right)+(1-v^2)\left(1-\frac{v}{r}\right)\right] \qquad (9.18)$$

Equation (18) can be rearranged in powers of r :

$$\sigma_s = \frac{1}{v_0^2}\frac{\pi^2}{8\lambda_b}\int_0^\infty dr\,\rho'(r)\int_{-1}^{1} du\int_{-1}^{1} dv\,(1-u^2)(1-v^2)\,\rho'(r+u+v)\times$$
$$\times\left\{(1-u^2)^2(1-v^2)+(1-u^2)(1-v^2)^2+\right. \qquad (9.19)$$
$$\left.+\frac{1}{r}\Big((1-u^2)(2u+v)+(1-v^2)(3u+2v)\Big)\right\}$$

There is a hidden symmetry between the two terms in the coefficient of r^0 . Consider one of these terms:

$$\int dr\int du\int dv\,\rho'(r+u+v)\,\rho_b(r+v)\,\rho'(r)\,(1-u^2)^2(1-v^2) \qquad (9.20)$$

(integration limits for r are unimportant providing that the gradient of the profile vanishes at them; limits for u and v are as in (19). Substituting $\xi = r+u+v$ for r in (20) yields

$$\int d\xi\int du\int dv\,\rho'(\xi)\,\rho_b(\xi-u)\,\rho'(\xi-u-v)\,(1-u^2)^2(1-v^2) \qquad (9.21)$$

Now substitute r for ξ then $-v$ for u and $-u$ for v to obtain

$$\int dr\int dv\int du\,\rho'(r)\,\rho_b(r+v)\,\rho'(r+u+v)\,(1-v^2)^2(1-u^2) \qquad (9.22)$$

which is exactly of the same form as the other coefficient of

r^0 in (19).

These two terms may now be added together and the expression for $\sigma_a'(r+u)$ introduced just as it was in (11). The resulting expression for σ_s is

$$\sigma_s = \frac{1}{v_0^2}\,\frac{\pi^2}{\lambda_b}\Big\{\frac{1}{3}\int dr\,\rho'(r)\int du\,\rho_b(r+u)(1-u^2)^2\sigma_a'(r+u)$$

$$+\frac{1}{8}\int dr\,\frac{\rho'(r)}{r}\int du\,\rho_b(r+u)\int dv\,\rho'(r+u+v)\times \tag{9.23}$$

$$\times\Big[(1-u^2)^2v(1-v^2)+(1-u^2)(2u+v)+(1-v^2)(3u+2v)\Big]\Big\}$$

In (23) terms of $O(r^{-2})$, which come from the expansion of $\sigma_a'(r+u)$, have been neglected.

We may now show that the leading order term in the coefficient of r^{-1} in the integral in (23) vanishes. The relevant term is, after simplification,

$$\int dr\,\frac{\rho'(r)}{r}\int du\,\rho_b(r+u)\int dv\,\rho'(r+u+v)(1-u^2)(1-v^2)\times$$
$$\times\Big[(1-v^2)(u+2v)+(1-u^2)(2u+v)\Big] \tag{9.24}$$

This has the same sort of symmetry as the leading term in (19) which can be exploited in a similar way. Putting $\xi = r+u+v$ in the first part of (24) to replace r yields

$$\int d\xi\int du\int dv\,\frac{\rho'(\xi-u-v)}{(\xi-u-v)}\,\rho_b(\xi-v)\,\rho'(\xi)\,(1-u^2)(1-v^2)^2\times \tag{9.25}$$
$$\times(u+2v)$$

On making the new substitutions, r for ξ, $-u$ for v and

$-v$ for u we have

$$\int dr \int du \int dv \; \frac{\rho'(r+u+v)}{(r+u+v)} \rho_b(r+v)\, \rho'(r)(1-u^2)^2(1-v^2) \times (-v-2u) \tag{9.26}$$

which to terms of $\mathcal{O}(r^{-1})$ is the negative of the second term in (24). Thus, the whole term vanishes to this order, as required

The remaining term in (23) can be reduced to a much simpler form by introducing the equation for the density profile (7.9). The surface tension then becomes (cf. (11))

$$\sigma_s = \frac{-\pi^2}{\upsilon_0^2 \lambda_b} \cdot \frac{1}{3} \int_{-\infty}^{\infty} dr\, \rho'(r) \int_{-1}^{1} du\, \rho_b'(r+u)(1-u^2)^2 \tag{9.27}$$

The gradients of all density profiles vanish at the limits on the r integration (last put in explicitly in (19)). Thus, an integration by parts yields

$$\sigma_s = \frac{\pi^2}{\upsilon_0^2 \lambda_b} \cdot \frac{1}{3} \cdot \int dr\, \rho(r) \int du\, \rho_b''(r+u)(1-u^2)^2 \tag{9.28}$$

A further integration by parts in the inner integral (limits as in (19) again) gives

$$\sigma_s = \frac{\pi^2}{\upsilon_0^2 \lambda_b} \cdot \frac{1}{3} \cdot \int dr\, \rho(r) \int du\, \rho_b'(r+u)\, 4u(1-u^2) \tag{9.29}$$

A second integration by parts in the r integral gives

$$\sigma_s = \frac{-\pi^2}{\upsilon_0^2 \lambda_b} \frac{4}{3} \int dr\, \rho'(r) \int du\, \rho_b(r+u)\, u(1-u^2) \tag{9.30}$$

Another in the u integral:

$$\sigma_s = \frac{\pi^2}{v_0^2 \lambda_b} \frac{4}{3} \int dr\, \rho'(r) \int du\, \rho_b'(r+u)\, u(1-u^2) \qquad (9.31)$$

A repetition of the sequence of integrations by parts applied to (31) as it was to (27) leads to

$$\sigma_s = \frac{3}{4} \int dr\, \rho(r) \int du\, (3u^2-1)\, \rho_b(r+u) \qquad (9.32)$$

where we have given v_0 its numerical value of $4\pi/3$. This expression for σ_s involves only the profiles themselves, not their derivatives and thus is more easily evaluated than, say (27), since the solutions to the equations for the density profiles yield only the profiles themselves in a numerical form. Of much more interest, however, is that (32) is formally identical to the equation for the surface tension of the planar surface (Leng, Rowlinson and Thompson, 1976). Thus, there is no <u>explicit</u> first order correction to the planar surface tension from this statistical mechanical route, in contrast to the result of thermodynamics (equation (2.26)). This correction is subsumed entirely in the departure in the form of the density profile from its limiting planar form. It is for this reason, among others, that so much care needs to be taken over the numerical solution of the equations for the drop density profiles. (The integral over u vanishes away from the interface where ρ_b is constant. Thus, all contributions to the integral over r in (20) come from around the interface as we should expect for any valid expression for the surface tension). In the next chapter (32) is used in a numerical calculation.

CHAPTER 10 SURFACE TENSION ESTIMATES

In this chapter the surface tension is obtained in the following ways:

(i) from (9.32) which is the form of the new statistical result (4.10) for this model,

(ii) from the thermodynamic formula (2.29), due to Tolman,

(iii) from a zero-temperature analysis of the free energy.

Of these only (iii) does not use the solution of the equation for the profile described in the previous chapter. It is also the only one which is free of the limitations imposed by the mean-field approximation (since it is exact at this temperature). All these results necessarily (see the discussion at the end of Chapter 2) give only an asymptotic correction to the large drop (planar) limit. We show that this correction is small and given to a close approximation by (i) to (iii) whenever they can be applied.

We may start with the low temperature solution. The limiting form of the density profile in a stepfunction,

$$\rho(R_c+r) = \begin{cases} \rho^\alpha & (r < R_c) \\ \rho^\beta & (r > R_c) \end{cases} \qquad (10.1)$$

Using (1) an explicit form for $\sigma^*(R_c+r)$ ((8.8), first part) may be obtained, at least for $R_c > 2$:

$$\sigma^*(R_c+r) = \begin{cases} \frac{3}{4}\rho^\beta\left(\frac{1}{3}(1+r)^2(2-r) + \frac{(1-r^2)^2}{4(R_c-r)}\right) + \\ +\frac{3}{4}\rho^\alpha\left(\frac{1}{3}(1-r)(2+r) - \frac{(1-r^2)^2}{4(R_c+r)}\right) \\ \qquad\qquad\qquad\qquad (|r| \leq 1) \\ \rho(R_c+r) \qquad\qquad\quad (|r| > 1) \end{cases} \qquad (10.2)$$

From its original derivation (Chapter 8) σ^* is directly related to the energy density, cf. (6.6) and (6.7). At the zero of temperature, however, the energy and free energy are identical and so we may use (2) to give the surface tension. The superficial energy density can be obtained from the energy density by subtracting off its homogeneous counterpart (cf. Leng, Rowlinson and Thompson, 1976, section 4):

$$\phi^s(R_e+r) = -\exp[-\sigma^*(R_e+r)] + \exp[-\rho'(R_e+r)] \qquad (10.3)$$

The total superficial energy, which is equal to the surface tension in this case, is given by integration of the energy density

$$\sigma(R_e) = \frac{1}{4\pi R_e^2}\int dr\,[4\pi(R_e+r)^2]\left\{e^{-\rho(R_e+r)} - e^{-\sigma^*(R_e+r)}\right\} \qquad (10.4)$$

The limits of integration are determined by the range of non-zero integrand from (2). Great simplifications can be achieved on inserting the zero-temperature limits: $\rho^\alpha \to \infty$, $\rho^\beta \to 0$, for a drop of the denser phase (rather than a bubble). The surface tension becomes

$$\sigma(R_e) = \int_0^1 dr\left(1-\frac{r}{R_e}\right)^2 - \int_{-1}^1 dr\left(1+\frac{r}{R_e}\right)^2 \exp\left(-\sigma^*(R_e+r)\right) \qquad (10.5)$$

Straightforward though involved algebra reveals that the largest contributions to the second integral vanish as $(\rho^\alpha)^{-1/4}$, leaving in the limit $\rho^\alpha \to \infty$:

$$\begin{aligned}\sigma(R_e) &= \sigma_s + \mathcal{O}\left(\frac{1}{R_e^2}\right) \qquad (10.6)\\ &= 1 + \frac{1}{R_e} + \frac{1}{3R_e^2}\end{aligned}$$

where the second line follows from (2.28).

Leng, Rowlinson and Thompson (1976) found the zero-temperature limit of the planar surface tension to be unity, thus (6) has the correct $R_e \to \infty$ limit. Comparison with Tolman's equation, (2.29), gives the limiting value of δ_∞ :

$$\underset{T\to 0}{\mathrm{lt}}\ \delta_\infty = -\frac{1}{2} \tag{10.7}$$

The sign of this quantity is not in agreement with most of the small number of previous estimates. For a Lennard-Jones fluid (cf. Rowlinson and Widom, 1982, (4.117)) a crude estimate gives δ , at all temperatures, a magnitude similar to that in (7), but with a positive sign - the one originally expected by Tolman. It is interesting that the sign of δ in (7) is in agreement with an estimate of the equivalent quantity for superfluid ^{4}He by Ebner and Saam (1975). We shall find that (7) is consistent with, and indeed a very good approximation to, numerical estimates at non-zero temperatures. It is therefore tempting to attribute this disagreement in sign to the form of the interaction potential (5.2) which is admittedly unrealistic though we know of no physical argument capable of predicting the sign of δ directly.

Tolman's equation, (2.29), shows that δ_∞ is the key to the variation of surface tension with size of drop at all temperatures. Although we cannot obtain this limiting value from a single calculated density profile, we can obtain $\delta = R_e - R_s$ (2.24) which, by assumption, will be a very good approximation to it. Therefore, with Laplace's equation for R_s and quadrature on the solution profile for R_e , Tolman's equation determines σ_s in terms of known quantities. We distinguish this 'thermodynamic' surface tension by the superscript ^{T} :

$$\frac{\sigma_\infty}{\sigma_s^T} = \frac{4\sigma_\infty \lambda_b}{R_e(\pi^\alpha - \pi^\beta)} - 1 \tag{10.8}$$

The planar limit of the surface tension required here is readily evaluated by the methods of Leng, Rowlinson and Thompson (1976).

A plot of σ_s^T from (8) versus R_e^{-1} at fixed λ_b is shown in Figure 8. Since only the term linear in R_e^{-1} from Tolman's equation is used in (8) this should be a straight line; the slight departures from linearity are the result of numerical errors.

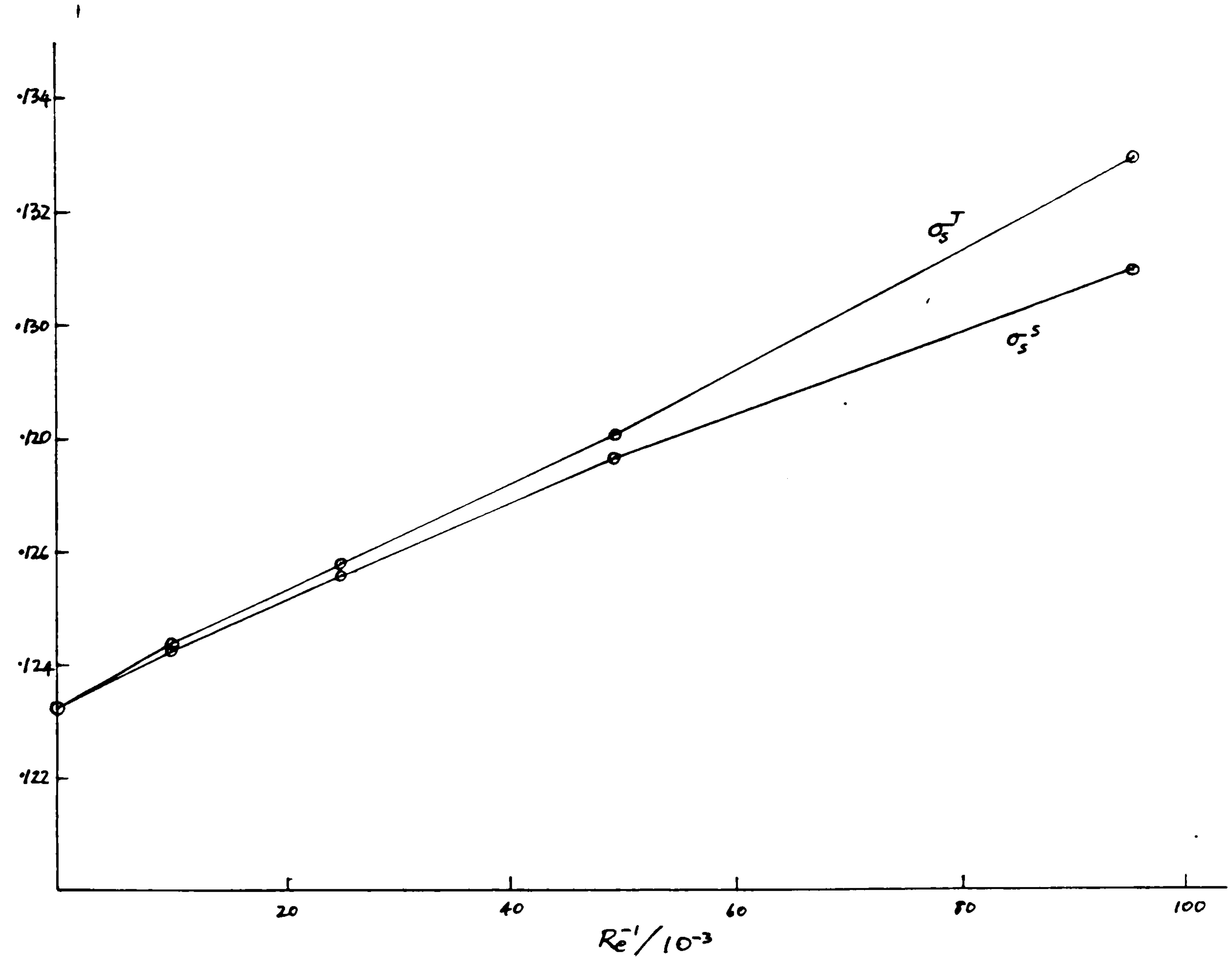
Figure 8 also contains plots of the quantity σ_s^S . This is the 'statistical' surface tension of Chapter 4 which is in terms of the density profiles from (9.32)

$$\sigma_s^S = \frac{3}{4\lambda_b}\int_0^\infty dr\, \rho_a(r) \int_{-1}^{1} du\,(3u^2-1)\,\rho_b(r+u) \tag{10.9}$$

We again distinguish the surface tension by this 'statistical' route by a superscript (^{S}). This surface tension also requires a knowledge of the numerical density profiles. Nevertheless a good agreement is obtained, both curves having, within numerical uncertainty, the same intercept and the same limiting slope.

A sensitive measure of the effect of curvature on surface tension may be estimated by calculating the quanitiy δ . This may be done either via the thermodynamic route (8) or

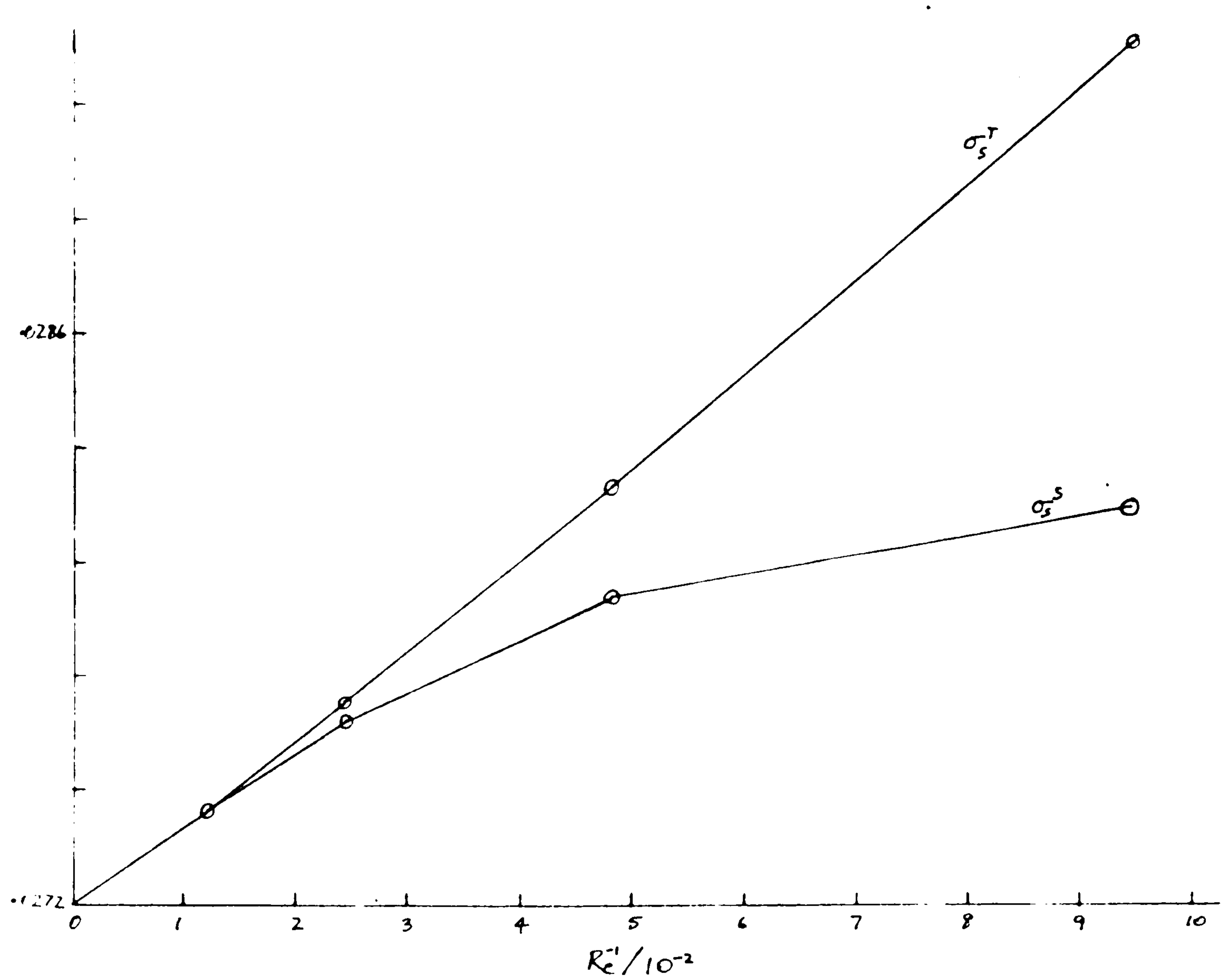
Figure 8a. Variation of surface tension with drop size



Both the 'thermodynamic' surface tension, σ_s^T, of (10.8) and the 'statistical' surface tension, σ_s^S, of (9.32) are shown. All calculations are for a temperature of 0.735 T_c (circles denote individual profiles). The planar limit, $Re \rightarrow \infty$, is independently calculated.

The slight departure from linearity in the points for σ_s^T is a consequence of numerical errors - the theory for this assumes that only this first order variation in Re^{-1} is significant.

Figure 8b. Variation of surface tension with drop size



The quantities shown are as those in the previous figure, at the higher temperature of 0.904 T_c . The disparity between the two two ways of calculating the surface tension is greater now, something which reflects the general trend. Note however that there is still good agreement in the asymptotic variation at large dropsize, this being the only variation of thermodynamic significance.

the statistical route (9). We denote these quantities δ^T and δ^S respectively. It is difficult to obtain either very accurately because the variation of the surface tension for drops well described by thermodynamics is very weak. The formal expression may be written down easily enough though:

$$\frac{R_e}{1+\delta^T} = \left(2 - \frac{R_e\,(\pi^\alpha - \pi^\beta)}{2\,\sigma_\infty\,\lambda_b} \right) \qquad (10.10)$$

this defines δ^T in terms of accessible quantities.

The variation of δ^T with temperature is shown in Figure 9. It is very weak and comparable with the 'scatter' of points due to numerical error, as can be seen from the figure. No systematic trend can be discerned;. these results show that the zero-temperature limit remains a good approximation for a wide range of temperatures. The variation of δ^S, defined as

$$\delta^S = R_e - \frac{2\,\sigma_s^S\,\lambda_b}{(\pi^\alpha - \pi^\beta)} \qquad (10.11)$$

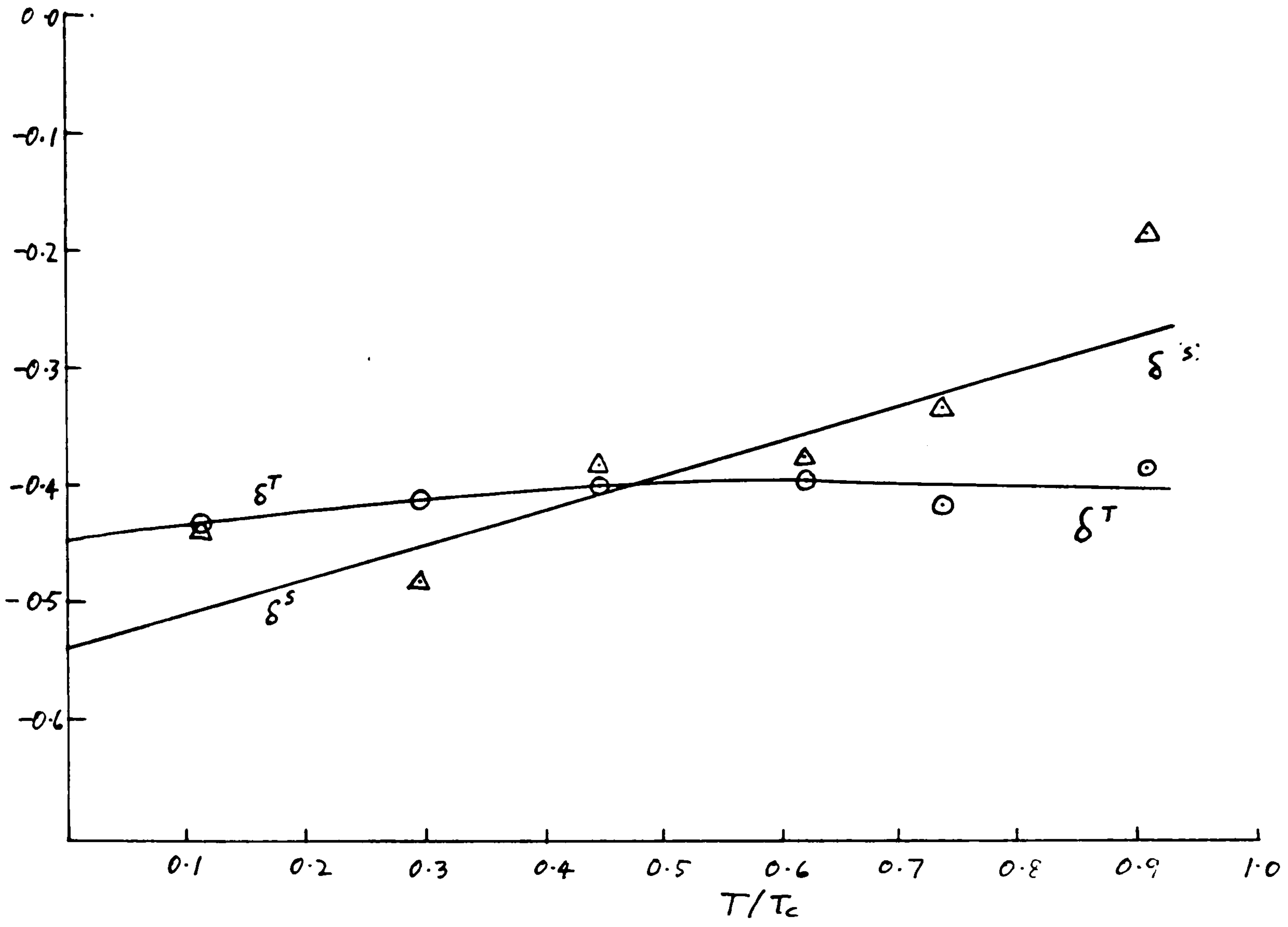
is also shown in this figure. It shows more scatter because of an extra numerical uncertainty in σ_s^S introduced in the double quadrature over the profiles in (9).

It is perhaps not obvious how (8),(10) or (11) have the correct large radius limit in which $\Delta\pi \to 0$. These equations all involve Laplace's equation, (7.7), which may be written

$$\lambda_b = \frac{(\pi^\alpha - \pi^\beta)\,R_s}{2\sigma_s} \qquad (10.12)$$

The left-hand side of this remains well-defined in the large radius limit so we have

Figure 9. Variation of 'Tolman's delta' with temperature



'Tolman's delta' is basically the separation of the equimolar surface and the surface of tension, (2.24), a quantity which governs the variation of surface tension with drop size - (2.26). Here, two measures, δ^T (10.10) and δ^S (10.11) are plotted for drops of about 20 reduced units in radius.

The circles denote calculations of δ^T , the triangles those of δ^S . Neither quantity can be estimated with great accuracy since each is given as the difference of two nearly equal quantities Nevertheless the zero-temperature limit above is entirely consistent with the independent analytic result (10.7).

$$\lambda_b = \underset{R_s, R_e \to \infty}{\mathrm{lt}} \frac{(\pi^\alpha - \pi^\beta)}{2\,\sigma_s} = \frac{1}{\sigma_\infty} \mathrm{lt} \frac{(\pi^\alpha - \pi^\beta) R_s}{2} \qquad (10.13)$$

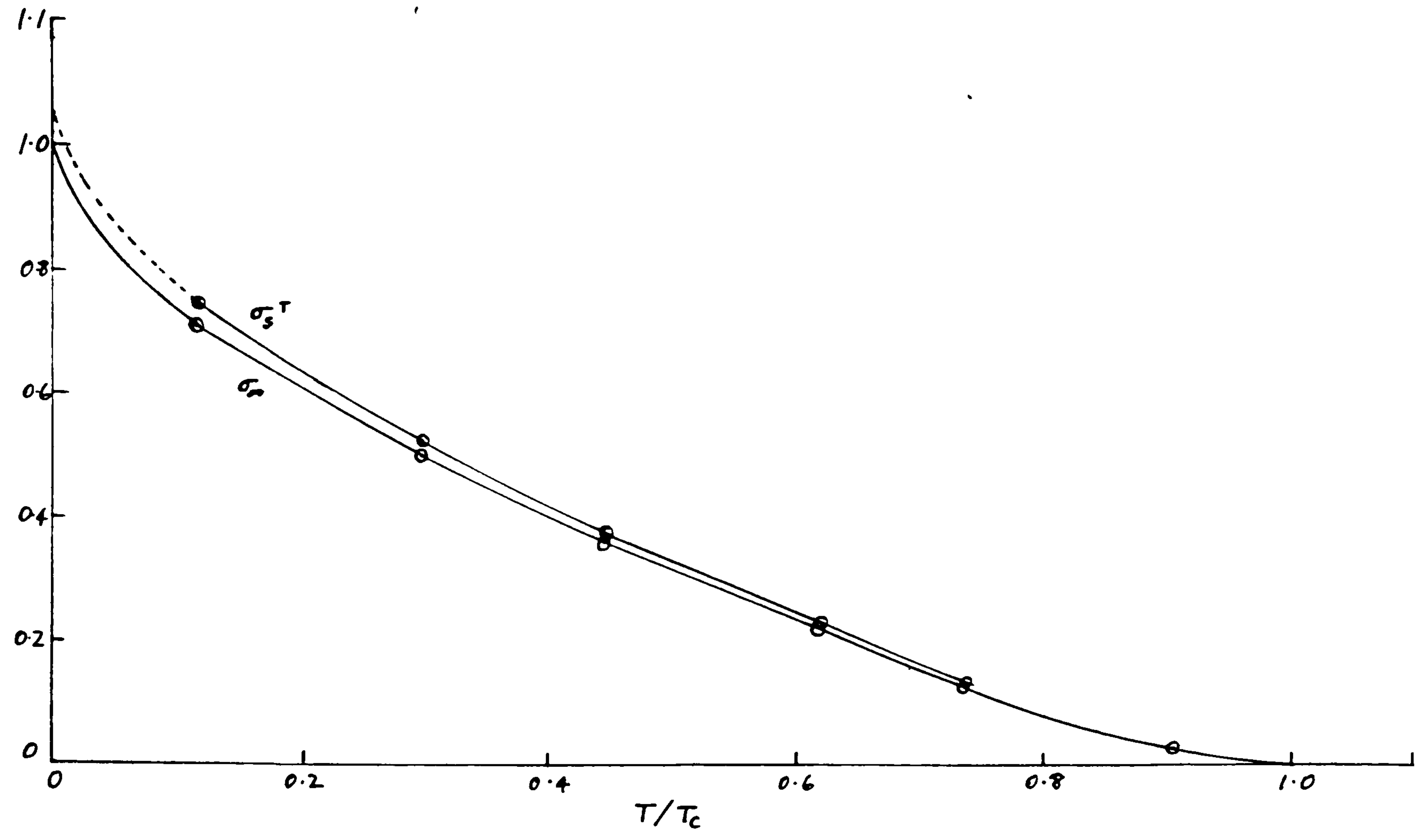
When this limit is introduced into (10), for example, it leads correctly to the identity

$$\underset{R_s \to \infty}{\mathrm{lt}} \delta^T = \underset{R_s \to \infty}{\mathrm{lt}} (R_e - R_s) \qquad (10.14)$$

The variation of δ^T and δ^S with temperature gives the variation of the rate of variation of surface tension with R_e. The variation of surface tension with temperature at constant dropsize contains less information though it can be readily calculated. As can be seen from Figure 10 it has a variation which is qualitatively identical to that of the planar surface tension which is also shown. Numerical calculations at very low values of the temperature are prohibited because the steepness of the profile necessitates an excessively small stepsize. Nevertheless, it can be seen that the zero-temperature limit, above, provides a very sensible extrapolation of the non-zero temperature results.

Surface tension is a thermodynamic quantity and therefore well-defined only for large systems. As we discussed at the end of Chapter 2, the surface tension of a drop is well-defined only to terms of order R_s^{-1}, as we find for all the results of the present chapter. Exact agreement between estimates for the surface tension of drops of a finite size, therefore, is an ideal which cannot be achieved. However, for 'moderate' dropsizes at which the thermodynamic limit has practically been reached, the sizes at which calculations have been done here,

Figure 10. Variation of surface tension with temperature



The upper curve shows the surface tension of a drop of about 20 units in radius. The calculations shown are of the 'thermodynamic' surface tension, σ_s^T, although on this scale the 'statistical' surface tension, σ_s^S, would be indistinguishable. The lower curve shows the planar surface tension, calculated independently.

The dotted line is one possible extrapolation to the zero-temperature limit given by (10.6).

different estimates for the surface tension can be meaningfully compared. The above comparisons are of this type, and within acceptable limits, show the statistical surface tension of Chapter 4 to be equivalent to the thermodynamic surface tension of Chapter 2. Although the mean-field approximation underlies all the results of this chapter, it is exact at the zero of temperature (Rowlinson, 1980, Chapter 3) and thus the analytic result, which yields a proper 'thermodynamic' expansion (6), is of particular importance. These results incidentally confirm that the position of the surface of tension defined by Laplace's equation is a well-defined quantity and therefore not subject to the uncertainty mentioned in Chapter 3 associated with expressions for it in terms of the pressure tensor. Although no analytic limit has been taken, the results for σ_s give no evidence to suggest that it is anything other than well-defined in the planar limit.

CHAPTER 11 APROXIMATIONS IN AN EQUATION FOR THE PLANAR DENSITY PROFILE

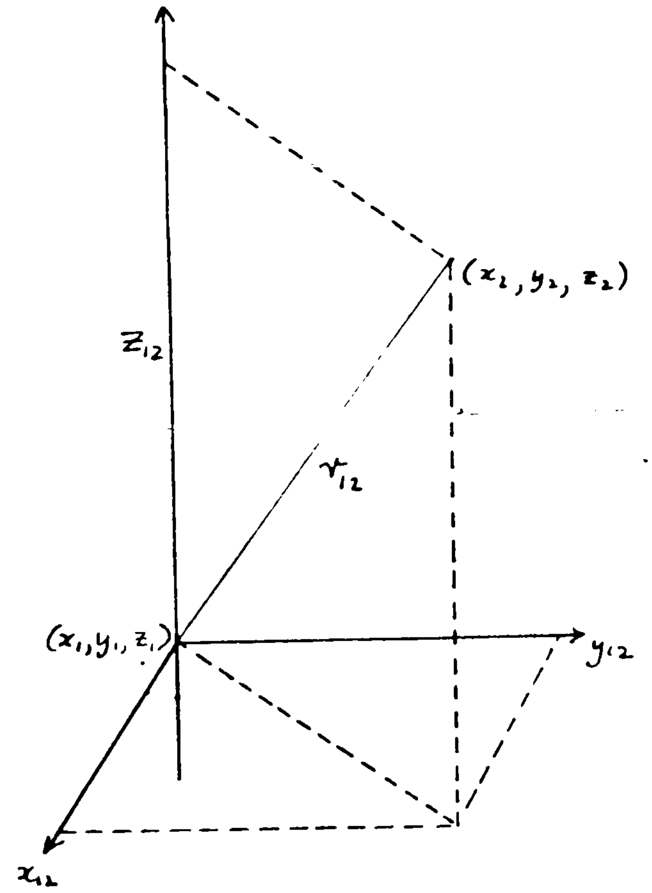
This chapter is concerned with finding a suitable approximate form for the quantity $c(\underline{r}_1, \underline{r}_2)$ in the general, exact equation (9.1). As usual the penetrable-sphere model will be used to obtain numerical results. It has the particular advantages that the quantity to be approximated, $c(\underline{r}_1, \underline{r}_2)$, and the quantity to be obtained, $\rho(z)$, are both known in the mean-field approximation (which we shall continue to employ). In this chapter a simple ansatz for the interfacial direct correlation function (idcf) will be constructed from general considerations. It will then be shown that a function of a very similar form can be deduced by making a physically reasonable simplification of the exact result for this particular model. The aim is to see if this simple ansatz can be used in (9.1) to produce an approximate density profile. It is well known that the corresponding procedure can be carried out for the BGY equation (see references in Chapter 13), but despite the close similarity of the equations this seems to be the first attempt of its kind.

The geometry of the system (Figure 11) reduces the number of independent variables on which the idcf depends to three, eg. z_1, z_{12} and r_{12}. The symmetry of the function $c(\underline{r}_1, \underline{r}_2) = c(\underline{r}_2, \underline{r}_1)$ requires that

$$c(z_1, z_{12}, r_{12}) = c(z_1 + z_{12}, -z_{12}, r_{12}) \qquad (11.1)$$

If we assume (following Pressing and Mayer, 1973) that the z_1, z_{12} dependence of the idcf may be represented by a Taylor series taken to first order, we have

Figure 11. Coordinate system for planar system.



The figure shows the three coordinates, z_1 , z_{12} and r_{12} which are sufficient to specify the direct correlation function, $c(\underline{r}_1, \underline{r}_2)$ in a system with planar symmetry. (The z axis is perpendicular to the interface.)

$$c(z_1+z_{12}, -z_{12}, r_{12}) = c(z_1, z_{12}, r_{12}) + z_{12}\frac{\partial}{\partial z_1}c(z_1, z_{12}, r_{12}) + (-2z_{12})\frac{\partial}{\partial z_{12}}c(z_1, z_{12}, r_{12}) \qquad (11.2)$$

Equation (1) then gives

$$\frac{\partial}{\partial z_1}c(z_1, z_{12}, r_{12}) = 2\frac{\partial}{\partial z_{12}}c(z_1, z_{12}, r_{12}) \qquad (11.3)$$

which requires that the idcf depend on z_1 and z_{12} only through the combination $(z_1 + z_{12}/2)$. We shall incorporate this result into our ansatz, but it should be noted that it depends on (2) which is valid only if all derivatives with respect to z_1 and z_{12} exist with those higher than the first being negligible. This condition will be satisfied, if at all, only when gradients through the interface are small - ie. near the critical point.

It seems a reasonable assumption that the idcf will resemble the ordinary bulk phase direct correlation function, $c(r;\rho)$. If this is so it should be possible to choose an effective density, ρ, such that

$$c(z_1, z_{12}, r_{12}) \approx c(r_{12}, \rho) \qquad (11.4)$$

We expect ρ to depend on z_1 and z_{12}; bearing in mind the result of the last paragraph we have the obvious, if restrictive, choice $\rho = \rho(z_1 + z_{12}/2)$. This, in principle, completely defines the ansatz. The problem is, however, that for a given sub-critical temperature this effective density will pass through the two-phase region of the phase diagram. Some attempt must therefore be made to interpolate into this region. We cannot give this problem the attention it deserves in this exploratory treatment but adopt the simple linear interpolation,

$$c(r,\rho) = \left(\frac{\rho_l-\rho}{\rho_l-\rho_v}\right)c(r,\rho_v) + \left(\frac{\rho-\rho_v}{\rho_l-\rho_v}\right)c(r,\rho_l) \qquad (11.5)$$

This is certainly not the best that can be done - eg. for the penetrable-sphere model the mean-field approximation can be used to obtain $c(r,\rho)$ right through the two-phase region - but it has the virtue of simplicity and generality. The general form of the ansatz is then

$$c(z_1,z_{12},r_{12}) \approx \frac{1}{\rho_l-\rho_v}\Big((\rho_l-\rho(z_1+z_{12}/2)\,c(r,\rho_v) + (\rho(z_1+z_{12}/2)-\rho_v)\,c(r,\rho_v)\Big) \qquad (11.6)$$

For the penetrable-sphere model substitution of the bulk phase dcfs into (6) gives

$$c(z_1,z_{12},r_{12}) = (\rho_l-\rho_v-\rho(z_1+z_{12}/2))\,f(r_{12}) \qquad (11.7)$$

where $f(r)$ is a polynomial giving the overlap volume of two unit spheres with their centres separated by r . It is interesting to compare (7) with the exact result (5.7). A detailed comparison is not feasible, but for a slowly varying density $\rho_b(\underline{r}_3)$ in the integral may be replaced by its value in the centre of the symmetrical domain $\tilde{v}$. Equation (5.7) then yields

$$c(z_1,z_{12},r_{12}) \approx \frac{\rho_b(z_1+z_{12}/2)}{v_0}\int_{\tilde{v}} d\underline{r}_3 = \rho_b(z_1+z_{12}/2)\,f(r_{12}) \qquad (11.8)$$

The symmetry condition (6.8)

$$\rho_a(z) = \rho_b(-z) \tag{11.9}$$

gives a new approximation for the dcf in terms of the density $\rho_a (= \rho)$:

$$c(z_1, z_{12}, r_{12}) \approx \rho(-(z_1 + z_{12}/2))\, f(r_{12}) \tag{11.10}$$

Leng, Rowlinson and Thompson (1976) were unable to get an analytic solution for the exact density profile but they did show that it was antisymmetric about the equimolar surface, ie. it could be written in the form

$$\rho(z - z_e) = \left(\frac{\rho_l + \rho_v}{2}\right) - g(z) \tag{11.11}$$

where $g(z) = -g(-z)$. Using this it can easily be shown that

$$\rho(-z) = \rho_l + \rho_v - \rho(z - 2z_e) \tag{11.12}$$

so that our approximation (10) becomes

$$c(z_1, z_{12}, r_{12}) = \left(\rho_l + \rho_v - \rho\left[-(z_1 + z_{12}/2) + 2z_e)\right]\right) \tag{11.13}$$

Now both the centre of symmetry, $z = 0$, and the equimolar surface lie in the interface itself; if they were coincident, ($z_e = 0$), the ansatz (13), which is essentially a limiting form of the exact idcf for this model, would be identical with the phenomenological ansatz (7). In fact z_e always lies in the interval $((3/20)^{\frac{1}{2}}, 1/2)$. At least at temperatures for which the interfacial thickness is several units we can be assured that, for this model, (6) gives a reasonable representation of the idcf. Whether this will be the case for any other model is extremely difficult to say (because of the extreme paucity of our detailed knowledge of correlations in the interface). However, there is no feature of the penetrable-sphere model which obviously makes (6) particularly suited to it.

We have now obtained our general ansatz (6), applied it to the model, (7), and confirmed that the result is not grossly inadequate by comparison with an independent result, (13). In the next chapter it is used to obtain the density profile.

CHAPTER 12 CALCULATION OF THE PLANAR DENSITY PROFILE

In the previous chapter an approximate form (ansatz) was constructed for the inhomogeneous direct correlation function, (idcf). This was obtained so that it could be substituted into the general equation for the density profile (9.1). In this chapter we investigate whether the resulting equation can be usefully solved.

Using the independent variables z_1 , z_{12} and r_{12} introduced above we may write (9.1) as

$$\rho'(z_1) = \rho(z_1)\int_{-\infty}^{\infty} dz_{12}\,\rho'(z_1+z_{12})\left\{\frac{2\pi}{v_0}\int_{|z_{12}|}^{\infty} dr_{12}\,r_{12} \times c(z_1, z_{12}, r_{12})\right\} . \qquad (12.1)$$

Here prime indicates differentiation. The first simplification to be carried out, when (11.7) is introduced, is to do the innermost integral analytically. This is straight-forward because the only r-dependence of the ansatz is in the simple polynomial $f(r)$. We define a function F as follows

$$F(x) = \frac{2\pi}{v_0}\int_{x}^{\infty} dr\, r\, f(r) \qquad (12.2)$$

The explicit form for $f(r)$ (Guerrero, Rowlinson and Sawford, 1974) yields

$$F(x) = \begin{cases} 3/5 - 3/4\, x^2 + 3/8\, x^3 - 3/160\, x^5 & (x \le 2) \\ 0 & (x > 2) \end{cases} \qquad (12.3)$$

We may now write (1) in a form which includes only a single integration:

$$\rho'(z_1) = \rho(z_1)\int_{-2}^{2} dz_{12}\,\rho'(z_1+z_{12}) \times \left(\rho_l+\rho_v-\rho(z_1+z_{12}/2)\right) F(|z_{12}|) \tag{12.4}$$

To solve this equation we follow the general strategy used by Toxvaerd (1975) and others - see eg. Croxton (1980, Chapter 2) - to solve the corresponding BGY equation. For a planar geometry this can be written

$$\rho'(z_1) = 2\pi\rho(z_1)\int_{-\infty}^{\infty} dz_{12}\,\rho(z_1+z_{12})\int_{|z_{12}|}^{\infty} dr_{12}\,r_{12} \times \left[\underline{\nabla}_1\,\phi(r_{12})\,g(z_1,z_{12},r_{12})\right] \tag{12.5}$$

where $\phi(r_{12})$ is the (pairwise) potential which acts between particles at positions $\underline{r}_1$ and $\underline{r}_2$. The term in square brackets, which is made up of the gradient of the potential and the inhomogeneous pair distribution function, depends only on z_1, z_{12} and r_{12} and so plays the same role as $c(z_1,z_{12},r_{12})$ in (1). Most solutions to (5), for a given ansatz for $g(z_1,z_{12},r_{12})$ proceed by integrating (5) with respect to z_1 from a point deep in the liquid:

$$\rho(z)-\rho_l = \int_{-\infty}^{z} dz_1\,2\pi\rho(z)\int dz_{12}\,\rho(z_1+z_{12})\int dr_{12}\,r_{12} \times \left[\underline{\nabla}_1\,\phi(r_{12})\,g(z_1,z_{12},r_{12})\right] \tag{12.6}$$

Successive substitution of an initial approximation $\rho_0(z)$ can then be used to obtain the solution $\rho(z)=\mathrm{lt}_{n\to\infty}\,\rho_n(z)$. Of course the process is not nearly as straight forward as this in practice, eg. it is frequently necessary to incorporate parameters into the ansatz solely for the purpose of facilitating convergence. In the procedure we describe below, however, the ansatz used is completely free from adjustable parameters and no scaling or shifting of the profiles is used as part of the iteration sequence.

The major difference between (1) and (2) as far as their solution is concerned is that (1) has the density gradient on its right-hand side, but (5) does not. It is therefore convenient to use a two-step iteration, dealing with the profile and its gradient in turn:

$$\rho_n(z) = \begin{cases} \rho^* + \int_{z^*}^{z} dz\, \rho'_n(z) & (z > z^*) \\ \rho^* - \int_{z}^{z^*} dz\, \rho'_n(z) & (z < z^*) \end{cases} \qquad (12.7)$$

$$\rho'_{n+1}(z) = \rho_n(z) \int_{-2}^{2} dz_{12}\, \rho'_n(z+z_{12}) \times$$
$$\times \left(\rho_l + \rho_v - \rho_n(z + z_{12}/2)\right) F(|z_{12}|) \qquad (12.8)$$

Equation (7) is simply obtained by integrating the gradient from an arbitrary reference density, $\rho^* = \rho_n(z^*)$. The choice of ρ^* is arbitrary providing that it does not lie outside $[\rho_v, \rho_l]$; in practice it was convenient to choose it to be $(\rho_l + \rho_v)/2$ so that z^* is always in the region of rapid density variation. This has the added advantage that it obviates the divergent behaviour frequently encountered in the solution of the corresponding BGY equation, (6), in which

$$\rho_n(z) \simeq \rho_{n-1}(z + \Delta) \qquad \Delta \neq 0 \qquad (12.9)$$

A Gaussian is a convenient choice for the starting approximation, $\rho'_0(z)$.

The above equations, (3), (7) and (8), constitute a complete specification of a procedure for solving the original equation (1). The program LMB in the Program Appendix has been written to perform these calculations. The discretization is handled as in Chapter 8: all quantities are held on a grid of stepsize H and the integration is carried out using a repeated Simpson's rule with this stepsize. The iteration sequence is modified to incorporate a relaxation parameter which can be varied to improve convergence. This is the only way in which the program departs from the above specification. The bulk phase densities, ρ_ℓ and ρ_v in (4), are taken from the mean-field equation of state of the model.

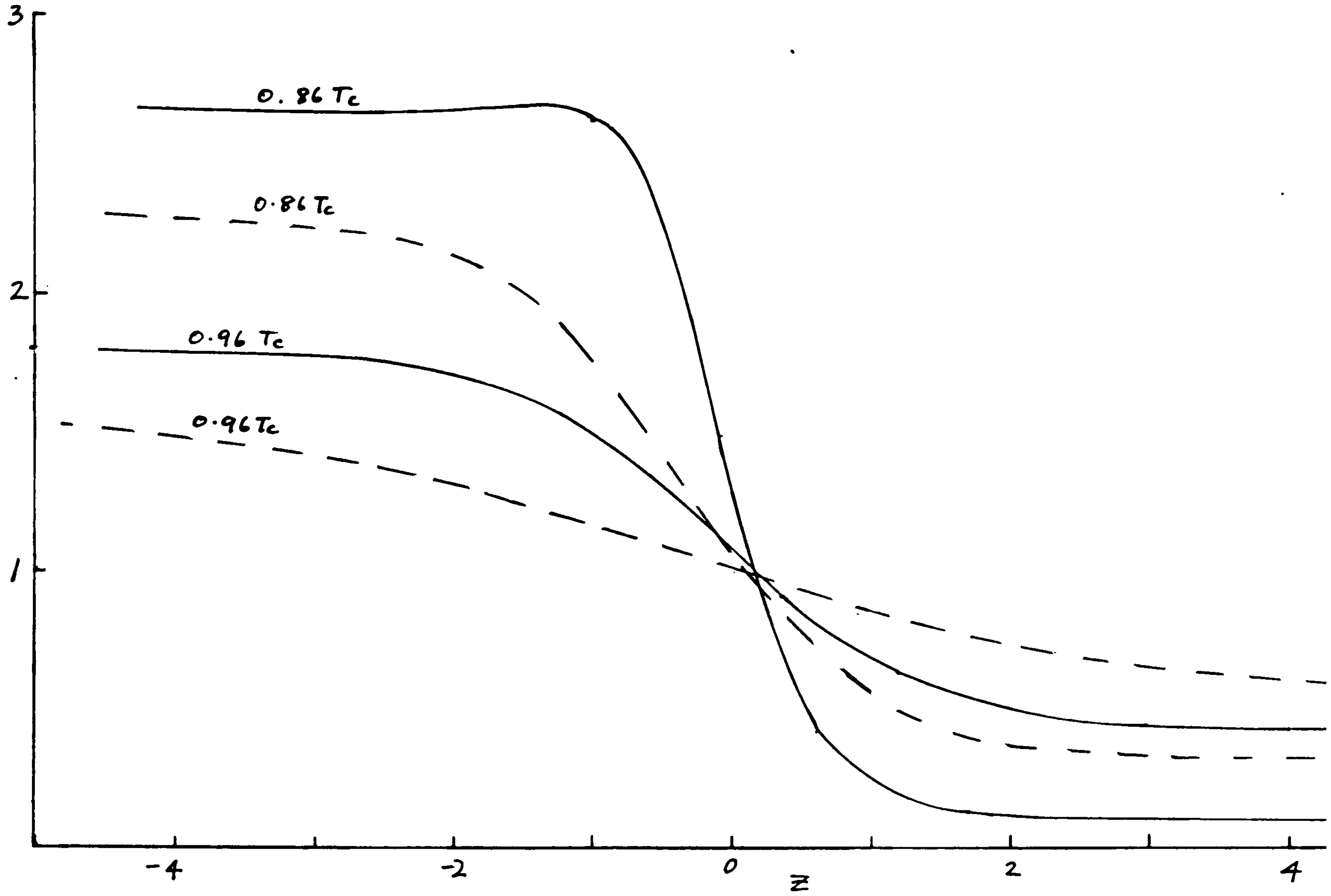
For a limited range of temperatures (down to $0.86\,T_c$) the iteration does converge to solutions of (1) which are recognisably density profiles. The procedure fails away from the critical point, as we might have anticipated, because the ansatz (11.6) is at best only a critical limit. As can be seen from Figure 12, a serious deficiency in the solution is the failure to get the bulk phase densities right. This is a common problem with the numerical solutions to the BGY equation, although the usual practice is to fix a priori the liquid density, as in (6), causing all the error to appear in the vapour density (which as a proprtion of this density can be very large indded). These errors in the bulk-phase densities are present even though the initial approximation has the correct limiting values

$$\mathop{\mathrm{lt}}_{z\to\infty} \rho_0(z) = \rho_\ell \quad ; \quad \mathop{\mathrm{lt}}_{z\to-\infty} \rho_0(z) = \rho_v \qquad (12.10)$$

The origin of this discrepancy is that (4) implies a relationship between ρ_ℓ and ρ_v , viz.:

$$\rho_v - \rho_\ell = \int_{-\infty}^{\infty} dz_1\, \rho(z_1) \int_{-\infty}^{\infty} dz_{12}\, \rho'(z_1+z_{12}) \times \left\{ \frac{2\pi}{\upsilon_0} \int_0^{\infty} dr_{12}\, r_{12}\, c(z_1, z_{12}, r_{12}) \right\} \qquad (12.11)$$

Figure 12. Approximate planar density profiles



The continuous curves show solutions of (12.4) for the density profile. The two curves, on the basis of the approximation for the direct correlation function, correspond to temperatures of 0.96 T_c and 0.86 T_c (as marked). The dotted curves show solutions of (6.11) - exact density profiles - at these temperatures.

which is consistent with the equation of state only when $c(z_1, z_{12}, r_{12})$ has the correct form all the way through the interface (not just in the bulk phases, like (11.7)).

Fischer and Methfessel (1980) have considered this question in connection with the BGY equation. They go as far as to say that this should be regarded as an eigenvalue equation in that non-trivial solutions for the density profile are possible only when the bulk phase densities and the ansatz are chosen consistently. They then abandon the use of a bulk-phase equation of state and vary one of the bulk densities until they obtain a convergent iteration sequence. Although the present equation can converge to the trivial solution $\rho(z) = \rho^*$, and frequently does so at low temperatures, varying ρ_l or ρ_v is not normally successful in generating a non-trivial solution.

Thus (1) can be used as a practical route to the density profile for a model fluid even if the simplest of approximations for the idcf, $c(z_1, z_{12}, r_{12})$, (11.7), is used. However, an inconsistency between this and the equation of state leads to errors in the asymptotes of the profile and (probably) prevents the sequence (7) and (8) converging at all, outside a fairly narrow range of temperature below the critical point. Rather than attempt to improve convergence by redefining the iteration sequence in an ad hoc way, we develop in the next chapter a systematic procedure for improving the basic ansatz.

CHAPTER 13 SELF-CONSISTENT APPROXIMATION FOR THE DIRECT CORRELATION FUNCTION

In the last chapter it was shown that the ansatz (11.7) was capable of yielding density profiles only in a limited region of the phase diagram. Moreover, the solutions themselves were inconsistent in that their asymptotic values away from the interface were different from the bulk phase densities ρ_l and ρ_v specified in the ansatz. It is this inconsistency which we seek to remove in the present chapter. We show that merely making a first order correction to (11.7), which is really a critical limit, yields a marked improvement in the quality of the solutions and the range over which they can be obtained.

The following procedure for obtaining the ansatz was suggested by Dr. J.R. Henderson to whom the author is indebted. The method is based on the use of 'sum-rules' for the coexisting densities in a liquid-vapour system proposed by Henderson and Lekner (1980) whose notation we follow here. A sum-rule may be obtained from our basic equation (12.1) by multiplication by $[\rho(z_1)]^{s-1}$ (s being arbitrary) followed by an integration over z_1 :

$$\frac{\rho_l^s - \rho_v^s}{s} = -2\pi \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_{12} \int_{|z_{12}|}^{\infty} dr_{12}\, r_{12}\, c(z_1, z_{12}, r_{12}) \times [\rho(z_1)]^s \rho'(z_1+z_{12}) \tag{13.1}$$

(here we temporarily drop the factor σ_0^{-1} which is needed only when the equation is written in penetrable-sphere model reduced units). In general if we introduce an approximation such as (11.7), which involves ρ_l and ρ_v , then the equality (1) will fail to hold. However, as we show later, we may write the ansatz in the form of an expansion about the critical point and then choose the coefficients so that (1) is satisfied to the appropriate (low) order. Then, to this order, the equation will be 'consistent' in the sense used above.

First we introduce a dimensionless function $\theta(z)$ which determines the form of the density profile:

$$\theta(z) = \frac{(\rho_l + \rho_v - 2\rho(z))}{\rho_l - \rho_v} \tag{13.2}$$

here ρ_l and ρ_v a priori are the large $|z|$ limits of the density profile, $\rho(z)$. We also introduce a dimensionless parameter, x, which vanishes at the critical point:

$$x = \frac{\rho_l - \rho_v}{\rho_l + \rho_v} \tag{13.3}$$

and an average density, $\bar{\rho}$:

$$\bar{\rho} = \frac{1}{2}(\rho_l + \rho_v) \tag{13.4}$$

Thus (2) becomes

$$\rho(z) = \bar{\rho}\,(1 - x\,\theta(z)) \tag{13.5}$$

In these variables the linear interpolation (11.5) becomes

$$\begin{aligned} c(z_1, z_{12}, r) = {} & \frac{1}{2}\left(c(r;\rho_l) + c(r;\rho_v)\right) - \\ & - \frac{1}{2}\left(c(r;\rho_l) - c(r,\rho_v)\right)\theta(\bar{z}) \end{aligned} \tag{13.6}$$

We will continue to use the result (11.4) and thus may take z in (6) equal to $z_1 + z_{12}/2$. Our aim is to improve on the above ansatz and so we introduce an extra term as follows

$$c(z_1, z_{12}, r) \approx \tfrac{1}{2}\left(c(r;\rho_l) + c(r;\rho_v)\right) - \\ -\tfrac{1}{2}\left(c(r;\rho_l) - c(r;\rho_v)\right)\theta(\bar{z}) \\ + a(x)\left(c(r;\rho_l) - c(r;\rho_v)\right)F(\theta) \qquad (13.7)$$

The function $F(\theta)$ is arbitrary except that it has the property that

$$F(\theta) = 0 \qquad (\theta = \pm 1) \qquad (13.8)$$

to ensure that (7) yields the correct bulk dcfs. The factor $c(r_{12},\rho_l) - c(r_{12},\rho_v)$ ensures that, provided $a(x)$ is well-behaved at $x=0$, the final term vanishes throughout the interface at the critical point itself. It is the primary object of this chapter to evaluate $a(x)$ which we assume can be represented by an expansion of the form

$$a(x) = a_0 + a_1 x + a_2 x^2 + o(x^2) \qquad (13.9)$$

The first step towards doing this is to rewrite (1) as an integral over r_{12} :

$$(\rho_l^s - \rho_v^s)/s = -\int_{-\infty}^{\infty} d\bar{z} \int d\underline{r}_{12}\, c(z_1, z_{12}, r_{12})\, \rho^s(z_1)\, \rho'(z_2) \qquad (13.10)$$

The integrand has a density-profile-dependent terms which may be written in terms of the new variables x , $\bar{\rho}$ and θ as follows

$$\rho^s(z_1)\rho'(z_2) = -\bar{\rho}^{s+1} x(1 - x\theta(z_1))^s \theta'(z_2) \qquad (13.11)$$

Now we may expand (11) about $\bar{z}$ obtaining an expression of the form

$$\rho^{s}(z_1)\rho'(z_2) = -\bar{\rho}^{s+1}x\left\{A + Bz_{12} + Cz_{12}^{2} + o(x^{3}) + o(z_{12}^{3})\right\} \tag{13.12}$$

The coefficients in this expansion can be written

$$A = \theta'(\bar{z})\left\{1 - sx\,\theta(\bar{z}) + \frac{s(s-1)}{2}x^{2}\theta^{2}(\bar{z})\right\} \tag{13.13}$$

$$B = -\frac{1}{2}\theta''(\bar{z})\left\{1 - sx\,\theta(\bar{z}) + s(s-1)x^{2}\theta^{2}(\bar{z})\right\} \tag{13.14}$$

$$C = \frac{1}{8}\theta'''(\bar{z})\left\{1 - sx\,\theta(\bar{z}) + s(s-1)x^{2}\theta^{2}(\bar{z}) + \frac{s(s-1)(s-2)}{6}x^{3}\theta^{3}(\bar{z})\right\} \tag{13.15}$$

Now if $c(z_1, z_{12}, r_{12})$ in (10) is replaced by the ansatz (7) it will only depend on r_{12} and $\bar{z}$, therefore all the odd powers of z_{12} in the expansion (12) will contribute nothing after integration and may be ignored from now on.

To proceed we must relate the behaviour of x and θ at the critical point. The key quantity here is the range of the dcf, ξ. This provides a unique length scale at the critical point (see Widom, 1973) and therefore determines the behaviour of the derivatives of θ and the range of the z_{12} integration. Classical critical point exponents can be used because we are considering the penetrable-sphere model in a mean-field approximation; the relevant asymptotic relations are ($\theta^{(m)} \equiv \frac{d^{m}\theta(z)}{dz^{m}}$, $\Delta t \equiv \frac{T-T_c}{T_c}$):

$$x \sim (\Delta t)^{1/2} \qquad (13.16)$$

$$\theta^{(m)} \sim \frac{1}{\xi^{m}} \sim (\Delta t)^{m/2} \qquad (13.17)$$

$$z_{12} \sim \xi^{m} \sim (\Delta t)^{-m/2} \qquad (13.18)$$

Consider the contribution from terms in equation (15) when (12) is taken under the integral sign in (10). The first two terms will vanish, eg. the second may be written

$$\int_{-\infty}^{\infty} d\bar{z}\ \theta'''(\bar{z})\,\theta(\bar{z}) = -\int_{-\infty}^{\infty} d\bar{z}\ \theta''(\bar{z})\,\theta'(\bar{z}) \qquad (13.19)$$

by parts; (19) becomes

$$-\int_{-\infty}^{\infty} d\bar{z}\ \theta''(\bar{z})\,\theta'(\bar{z}) = -\frac{1}{2}\Big[\theta'(\bar{z})\Big]_{-\infty}^{\infty} = 0 \qquad (13.20)$$

The first non-zero term in (15) is thus of order $\theta'''(\bar{z})x^{2}$ which by (16) and (17) vanishes as x^{5} . By similar arguments it is easy to show that the coefficients (D, E, F etc.) of all higher powers of z_{12} in the expansion (12) vanish as x^{3} or quicker when it is used with (10).

Having dealt with the term $\rho^{S}(z_1)\rho^{l}(z_2)$ we now consider $c(z_1, z_{12}, r_{12})$, or rather the ansatz for this, (7). In this the only radial dependence is contained in the bulk dcfs and so the integral over r_{12} in (10).may be evaluated provided the zeroth moments of these functions are known. Guererro, Rowlinson and Sawford (1974) have obtained the latter, which may be expressed in terms of the present notation as follows

$$\int d\underset{\sim}{r}\; c(r, \rho_v) = \frac{1}{\bar{\rho}}\left\{1 - x + \frac{2x^3}{3}\right\} \tag{13.21}$$

$$\int d\underset{\sim}{r}\; c(r, \rho_\ell) = \frac{1}{\bar{\rho}}\left\{1 + x + \frac{2x^3}{3}\right\} \tag{13.22}$$

With these expressions (10) can be simplified to the extent that it involves only a one-dimensional integral:

$$\begin{aligned}\frac{\rho_\ell^s - \rho_v^s}{s} = {} & \bar{\rho}^s x \int d\bar{z}\left[\theta' - s x\theta\theta' + s(s-1)x^2\theta^2\theta'\right] \times \\ & \times\left[\left(1 + \frac{2x^2}{3}\right) + x\theta + a(\dot{x})'(-2x)\, f(\theta)\right]\end{aligned} \tag{13.23}$$

(here $\theta = \theta(\bar{z})$, $\theta' = \theta'(\bar{z})$). If we define moments of F by the integrals

$$F_n = \int_{-1}^{1} d\theta\, \theta^n F(\theta) \tag{13.24}$$

then (23) becomes, with (9),

$$\begin{aligned}\frac{\rho_\ell^s - \rho_v^s}{s} = {} & \bar{\rho}^s x\Big\{\left[2 + \tfrac{4}{3}x - 2a_0F_0x - 2a_0F_0x^2\right] \\ & + s\left[-x^2 - 2a_0F_1x^2\right] \\ & + s^2\left[x^2/3\right] + \mathcal{O}(x^4)\Big\}\end{aligned} \tag{13.25}$$

We have finally reached our goal of expressing the right-hand side as an expansion in powers of s and x. The left-hand side may also be expanded in terms of s and x:

$$\frac{\rho_\ell^s - \rho_v^s}{s} = \bar{\rho}^s\left(2x + \frac{(s-1)(s-2)}{3}x^3 + \mathcal{O}(x^4)\right) \tag{13.26}$$

Equations (25) and (26) may be equated term-by-term for all powers of x and s. The resulting equations determine the first two coefficients in (9), which are found to be

$$a_0 = 0 \quad ; \quad a_1 = 1/3F_0 \tag{13.27}$$

With these (7) can be used to provide a new ansatz once some simple choice for the arbitrary function $F(\theta)$ is made. Reverting to familiar penetrable-sphere model variables (7) becomes, with $F(\theta) = \theta^2 - 1$,

$$c(z_1, z_{12}, r_{12}) = \Big[\rho_l + \rho_v - \rho(\bar{z}) - \frac{(\rho(\bar{z}) - \rho_v)(\rho_l - \rho(\bar{z}))}{(\rho_l + \rho_v)} \Big] f(r_{12}) \tag{13.28}$$

which is, as we should expect, equal to the ansatz previously obtained, (11.7), with an additional term which vanishes away from the interface.

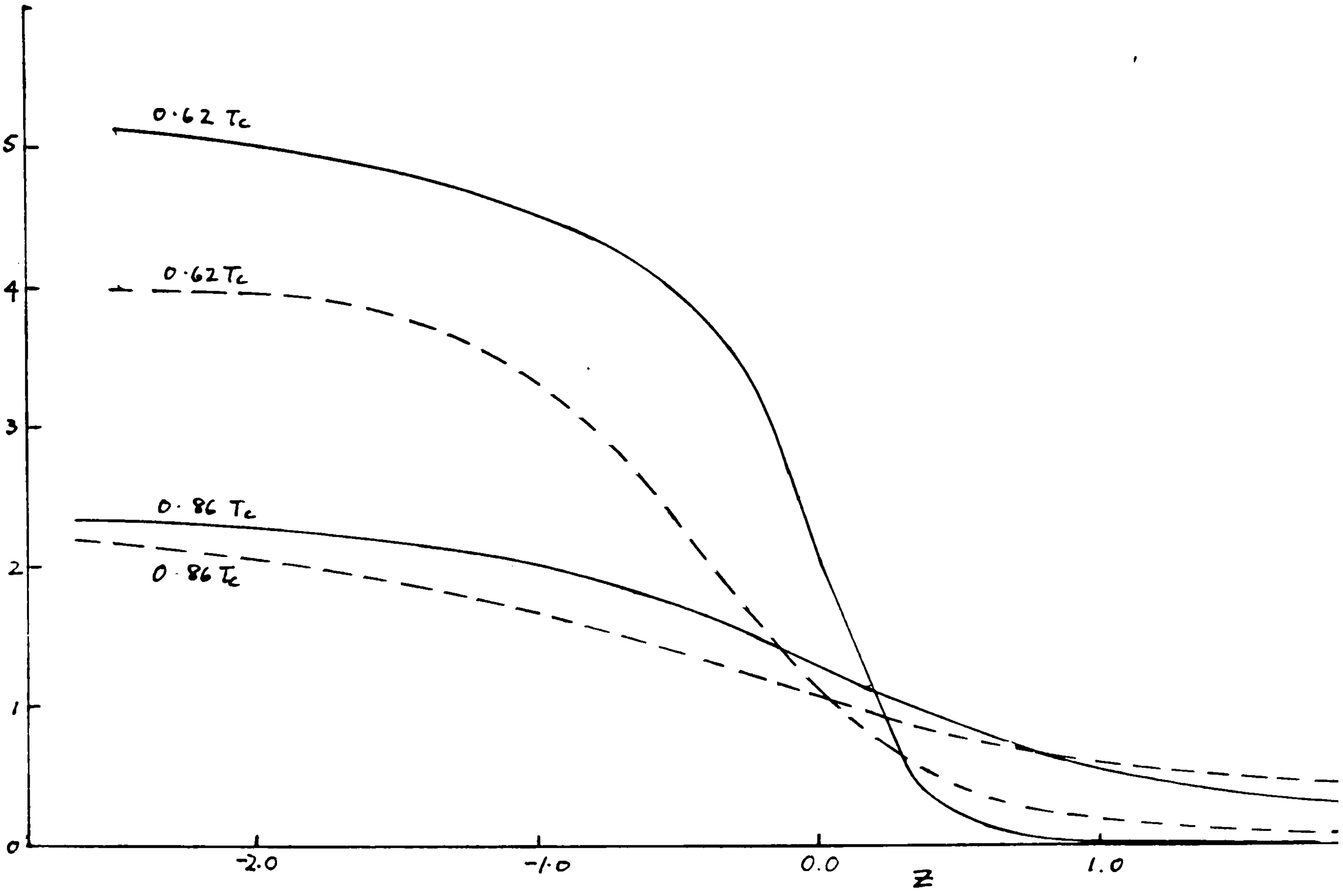
Following the notation of Chapter 12, the new form of the equation for the profile is

$$\rho'(z_1) = \rho(z_1) \int dz_{12}\, \rho'(\bar{z}) \Big(\rho_l + \rho_v - \rho(\bar{z}) - (\rho(\bar{z}) - \rho_v) \times \times \frac{(\rho_l - \rho(\bar{z}))}{(\rho_l + \rho_v)} \Big) \times F(|z_{12}|) \tag{13.29}$$

the function $F(|z_{12}|)$ is now as defined in (12.3) (not $F(\theta)$ used above). This solution may be solved by precisely the same algorithm described in the previous chapter. The basic inputs to the program LMB (which may be modified to solve (29) with only trivial changes) are again ρ_l and ρ_v but now they represent both the thermodynamically coexisting densities, used as parameters in the ansatz (28) and, to a good approximation, the asymptotic limits of the density profile. A much wider range of solutions may now be obtained (solutions down to $T = 0{\cdot}52\,T_c$ present no difficulty). Two solutions are shown in Figure 13; the exact (mean-field) solution (which is a solution to the equation (6.11) calculated by the method of Leng, Rowlinson and Thompson, (1976)) is also shown for comparison. As can be seen, there is a very marked improvement compared with the earlier solutions (Figure 12).

These results show that by making minimal assumptions about the form of an ansatz for the idcf, as in (11.6), we can obtain solutions to the general equation for the density profile, (12.1), without undue difficulty. This is much facilitated, however, if steps are taken to ensure that the ansatz is chosen consistently in the sense of this chapter. This has, to a limited extent, been appreciated in the closely analagous case of the BYG equation (Fischer and Methfessel, 1980), although they achieve their consistency by a trial and error method at the stage of solving the equation. Although the present method is probably to be preferred it does require a rather detailed knowledge of the behaviour of the bulk dcfs near the critical point ((21) and (22)). Because we cannot readily extend the present method to systems more realistic than the penetrable-sphere model, in the next chapter we revert to the method of Chapter 11 to attempt to obtain the density profile of a Lennard-Jones fluid in the hope that at least the limited success for the penetrable-sphere model can be repeated.

Figure 13. Approximate planar density profiles



The figure shows two typical profiles obtained by the new method, i.e. two solutions of (13.29). 'Exact' profiles at corresponding temperatures are also shown.

CHAPTER 14 CALCULATIONS FOR A LENNARD-JONES FLUID

In this chapter we shall turn our attention briefly to a new model, the Lennard-Jones 12-6 fluid. Essentially we repeat the analysis of Chapters 11 and 12 for this new model; as was explained in the last chapter the more sophisticated analysis used there for the penetrable-sphere model cannot easily be extended. The new model has a potential interaction of the form

$$U(\underline{r}_1, \ldots \underline{r}_N) = \sum_{i>j}^{N} V(r_{ij}) \qquad (14.1)$$

with $r_{ij} \equiv |\underline{r}_i - \underline{r}_j|$; the pair potential $V(r)$ is given by

$$\frac{V(r)}{kT} = \frac{4}{T^*}\left(r^{-12} - r^{-6}\right) \qquad (14.2)$$

The unit of length is determined by this potential, $V(1) = 0$; T^* is a dimensionless temperature characterising the model.

As in earlier chapters the calculation separates into two parts. First a suitable ansatz for the inhomogeneous direct correlation function is constructed, then the equation which results from substituting this into the general equation for the density profile,

$$\rho'(z_1) = 2\pi\,\rho(z_1)\int_{-\infty}^{\infty} dz_{12}\,\rho'(z_1+z_{12})\int_{|z_{12}|}^{\infty} dr_{12}\,r_{12}\,c(z_1, z_{12}, r_{12}) \qquad (14.3)$$

is used to set up an iterative sequence.

Our basic ansatz (11.6) is used for the first stage. Now, however, an approximation has to be devised for the bulk dcfs $c(r, \rho_L)$ and $c(r, \rho_V)$. We can afford to make our choice largely on the basis of analytic convenience since it is likely that the errors inherent in (11.6) will swamp those in any respectable theory for these bulk properties. The iterative method of Chapter 12 may be then used to solve the resulting equation.

The bulk dcf we use may be written

$$c(r;\rho) = \begin{cases} \alpha + \beta r + \gamma r^3 & (r \leq 1) \\ \exp(-V(r)/kT) - 1 & (1 < r < r_c) \\ 0 & (r > r_c) \end{cases} \qquad (14.4)$$

This is based on an analytic fit to the bulk phase dcfs obtained by numerical solution of the Percus-Yevick equation given by Ebner, Saam and Stroud (1976). In (4) α , β and γ are the coefficients obtained by Wertheim (1968) in his analytic solution to the Percus-Yevick equation for hard spheres:

$$\alpha = -(1-2\eta)^2/(1-\eta)^4 \qquad (14.5a)$$

$$\beta = 6\eta(1-\eta/2)^2/(1-\eta)^4 \qquad (14.5b)$$

$$\gamma = -\eta(1-2\eta)^2/(2(1-\eta)^4) \qquad (14.5c)$$

where $\eta = \frac{\pi\rho}{6}$. . The second term is simply the Mayer f-function: the low density limit of the dcf. The cut-off distance, r_c , was taken as 2.5.

The ansatz (11.7) may now be introduced, yielding an equation for the profile which may be written

$$\rho'(z_1) = \frac{2\pi\rho(z_1)}{(\rho_l-\rho_v)} \int_{-r_c}^{r_c} dz_{12}\, \rho'(z_1+z_{12}) \times \times \left[\rho(\bar{z})\, F(|z_{12}|) + Q(|z_{12}|)\right] \tag{14.6}$$

where, as usual, $\bar{z} = z_1 + z_{12}/2$. F and Q are functions defined by

$$F(x) = \int_x^{r_c} dr\, r \left(c(r;\rho_l) - c(r;\rho_v)\right) \tag{14.7}$$

$$Q(x) = \int_x^{r_c} dr\, r \left(\rho_l c(r;\rho_v) - \rho_v c(r,\rho_l)\right) \tag{14.8}$$

These may be evaluated numerically in a single calculation and stored as a table of values for use in the iterative procedure. These calculations are performed by LJLMB, listed in the Program Appendix, which us closely related to the program LMB used to solve the penetrable-sphere model equation corresponding to (6), viz. (12.4). Unfortunately for no combination of input parameters could any convergence be obtained.

Three variants on the original method were also tried in an attempt to solve (6). In one of these the suggestion of Co, Kuzak and Luks (1977), originally made in connection with the BGY equation for a square-well fluid, was used. In this method (12.7) was replaced by the more symmetrical form:

$$\rho_n(z) = \frac{1}{2}(\rho_l + \rho_v) + \frac{1}{2}\left[\int_{-\infty}^{z} dz\, \rho_n'(z) - \int_{z}^{\infty} dz\, \rho_n'(z)\right] \tag{14.9}$$

(it is of course an average of two versions of (12.7), one with $\rho^* = \rho_v$, the other with $\rho^* = \rho_l$). Despite the virtues claimed for this form no improvement resulted from its use; nor did any from the use of (12.7) with $\rho^{*}=\rho_v$ or $\rho^{*}=\rho_l$ separately ('normally' $\rho^{*}=(\rho_l+\rho_v)/2$, cf. remarks following (12.7)).

The next variant dispensed with the linear interpolation of (11.7) entirely and instead used the density variation implicit in (4) directly:

$$c(z_1, z_{12}, r_{12}) = c(r_{12}\, ;\, \rho(\bar{z})) \tag{14.10}$$

(this procedure is not justified by the numerical solutions of Ebner, Saam and Stroud (1976) because these were confined to the stable and meta-stable parts of the phase diagram). This technique gives rise to no apparant improvement in the convergence properties.

Up to now only iterative attempts to solve integral equations have been made. These have the disadvantage that they can fail to converge both for 'physical' reasons which make the problem ill-posed and for purely mathematical reasons such as the choice of an inadequate starting approximation. Therefore, an attempt was made to solve (6) by a variational method based on the single parameter function

$$\rho(z,\lambda) = \begin{cases} \rho_v + \dfrac{(\rho_l-\rho_v)}{2} \exp(-z/\lambda) & (z \geq 0) \\ \rho_l - \dfrac{(\rho_l-\rho_v)}{2} \exp(-z/\lambda) & (z < 0) \end{cases} \tag{14.11}$$

If $\rho(z,\lambda)$ represents the exact solution then the quantity $\delta(\lambda)$,

$$\delta(\lambda) = \int_{-\infty}^{\infty} dz \left| \rho'(z,\lambda) - \rho(z,\lambda) \int_{-\infty}^{\infty} dz_{12}\, \rho'(z+z_{12},\lambda) \int_{|z_{12}|}^{\infty} dr\, r\, c(r, z, z_{12}) \right. \tag{14.12}$$

will vanish identically. Calculations performed by the program

LMBFIT (to be found in the Program Appendix), with the ansatz for $c(z_1,z_2,r_{12})$ as in (6), reveal that $\delta(\lambda)$ has a monotonic behaviour for all physically reasonable values of λ . This shows that (11) cannot be made a good approximation to the solution of (6) by varying λ .

These results indicate that our general strategy, based on (11.7) is not readily capable of producing density profiles for the Lennard-Jones fluid (although there may be values of (ρ^l,ρ^v,T^*) for which calculations have not yet been made which are capable of yielding a solution). The point at which the procedure breaks down cannot be identified unambiguously, although suspicion must be centred around (11.7) which we found to enjoy limited success even with the penetrable-sphere model. A repeat of the analysis of Chapter 13, in which it was shown that a small modification to the ansatz gave much improved density profiles would confirm this. Unfortunately, this cannot be carried out because the analogues of (13.21) and (13.22) are not available. If the fault does lie with the ansatz it might be possible to incorporate some correction to it whose value could be optimized in order to ensure convergence to a profile of the correct general form (eg. having the correct bulk phase densities). It is felt that this procedure is dangerous, however, because it is capable of generating profiles which are arbitrarily 'correct' without yielding any insight into the physical behaviour of the idcf.

APPENDIX

In this Appendix we describe two computational aspects of the solution to the integral equation of Chapter 8 which were only briefly referred to there. One is a method for accurately computing the position of the equimolar surface using floating point arthimetic and the other is a special optimization procedure which takes into account the unusual nature of the function $Q^{(n)}$ ((8.14) and (8.15)) to be minimised.

The definition of the position of the equimolar surface, R_e, in a spherical system may be written

$$\int_{R^\alpha}^{R_e} d(r^3)\left(\rho(r)-\rho^\alpha\right) + \int_{R_e}^{R^\beta} d(r^3)\left(\rho(r)-\rho^\beta\right) = 0 \qquad \text{(A1)}$$

where R^α and R^β are positions deep in the bulk phases. Formally R_e may be obtained in terms of an integral over the density profile:

$$R_e = \left\{\frac{1}{\rho^\alpha-\rho^\beta}\int_{R^\alpha}^{R^\beta} d(r^3)\rho(r) + (R^\alpha)^3\rho^\alpha - (R^\beta)^3\rho^\beta\right\}^{1/3} \qquad \text{(A2)}$$

If $\rho(r)$ is specified at intervals H, from the solution of the integral equation of Chapter 8, R_e may be estimated from (A2) after doing the appropriate quadrature. If H is small or $(R^\alpha-R^\beta)$ is very large this estimate can be affected by rounding errors, both in the quadrature and in taking the difference of large numbers in (A2).

These errors can be avoided by evaluating the quantity, M,

$$M = \int_{R^\alpha}^{R_m} d(r^3)\left(\rho(r)-\rho^\alpha\right) + \int_{R_m}^{R^\beta} d(r^3)\left(\rho(r)-\rho^\beta\right) \qquad \text{(A3)}$$

where R_m is an arbitrary point in or near the interface. The form of the integral ensures that it is in fact independent of R^α and R^β. (A3) may be used with (A1) to yield a simple formula for R_e :

$$R_e = \left(\frac{M}{\rho^\alpha - \rho^\beta} + R_m^3 \right)^{1/3} \qquad \text{(A4)}$$

The next part of the Appendix concerns the algorithm used to find the smallest value of $Q^{(n)}$ of Chapter 8. This is a number which indicates how far from convergence a given profile is after it has 'asymptotically converged' at a given value of $R_e^{(0)}$ - $Q^{(n)}$ thus depends on $R_e^{(0)}$. The feature of the calculation which makes it difficult to do this minimisation is that the calculation of $Q^{(n)}$ at different values of $R_e^{(0)}$ cannot be done simultaneously, instead a sequence of values is generated, the initial approximation used for a new value of $R_e^{(0)}$ being the asymptotically converged profile at the previous one.

In the following algorithm the procedure funct does a single iteration, at a given value of $R_e^{(0)} (\equiv rm)$ returning a value $Q \; (\equiv Q^{(n)})$. Every time funct is called it updates a copy of the density profile, which it retains, which was calculated on its last call. (It is an 'abnormal' function, or function with 'side-effects' in computer-science terminology). The algorithm determines whether the iteration has asymptotically converged by determining two successive values of $Q^{(n)}$ (q and ql)) calculated at the same value of rm . Once asymptotic convergence has been reached rm is incremented by an amount drm , the last value of ql stored in qlo , and new values of q and ql are found. This procedure is repeated until the increment in rm results in an increase in the value of the (asymptotically converged) value of q . The increment is then reduced to a fraction of its former value and changed in sign and the whole procedure repeated. Eventually q drops below some preset small quantity eps and the profile is accepted.

The flow of control of the algorithm is determined by comparisons of the values stored in q , ql and qlo . These can only be initialised by calls of the function funct in the correct sequence. In order to prevent the comparison of un-initialised values each variable is given a logical tag which is set to true when the variable has been initialised and false otherwise.

In ALGOL60 syntax the algorithm is given on the following page.

```
procedure minimize (funct, rm, factor, eps, drm, repeat);
value factor, eps, repeat;
procedure funct;
real rm, factor, eps, drm;
integer repeat;
  begin
  Boolean qknown, qlknown, qloknown;
  real q, ql, qlo;
  integer i, dummy;
  for dummy := 1 while q > eps do
    begin
    qknown := qlknown := qloknown := false;
    for i := 1 step 1 until repeat do
      begin
      if qknown and qlknown and q > ql then
        begin
        if qknown and ql > qlo then drm := -drm/factor;
        rm := rm + drm;
        qlo := ql;   qlknown := true;
        qlknown := qlknown := false;
        end;
      if qknown then
        begin
        ql := q;   qlknown := true;
        end;
      funct(rm, q);   qknown := true;
      end
    end
  end;
```

SUPPLEMENTARY APPENDIX ON THE MEAN-FIELD APPROXIMATION

In a mean-field approximation each molecule experiences a uniform background potential made up of interactions with a large number of others. Physically this means that the resultant of the intermolecular forces will be small, i.e. the gradient of the interaction potential will tend to zero (hence the term 'mean-field'). Clearly the corollary of this is that the intermolecular potential, or at least that part of it to which the approximation is applied, will not be structure-determining. This may be used as a starting point from which to apply the approximation, as in the Bragg-Williams theory of alloys, though, as we shall see, it is not the only one.

It is instructive to consider situations in which the approximation becomes exact. One of the best known mean-field theories of fluids is the type of equation of state named after van der Waals. Kac, Uhlenbeck and Hemmer (1963) showed that such an equation of state, complete with Maxwell construction, could be obtained as an exact consequence of the assumption of an intermolecular pair potential of a particular infinitely long-ranged form. For this type of model each molecule will interact with infinetly many others even in the one-dimensional system which Kac et al. considered, thereby satisfying the requirement of an mfa mentioned above. It might be thought that a long-ranged intermolecular potential would always be required; if we are prepared to consider systems of arbitrary dimensionality, d, however, we can achieve the same effect by taking the $d \to \infty$ limit even when the model has only short-ranged interactions. This can be done both for the Ising model by varying the coordination number (Widom, 1982) and for the penetrable-sphere model by generalizing the definition of the intermolecular separation, r , in (5.1). The big advantage of such an approach is that the mfa for finite dimensionality becomes identical to an exact model - one with a well defined Hamiltonian - of infinite dimensionality. This is the origin of the consistency of the model discussed in Chapter 5.

By taking the $d \to \infty$ limit of the graphical expansion of the equation of state of the primitive version of the penetrable-sphere model, Guerrero, Rowlinson and Sawford (1974) were able to show that the equation of state is truncated at the second virial coefficient, (5.4d):

$$\pi^{(2)} = \rho_a + \rho_b + \rho_a \rho_b \qquad (1)$$

They were similarly able to find the energy density in the transcribed version, (5.6):

$$\phi = 1 - \rho - e^{-\rho} \qquad (2)$$

This had previously been derived as a consequence of the assumption that penetrable spheres took up a random configuration in a homogeneous system, confirming that this assumption is rigorously equivalent to taking the $d \to \infty$ limit in this case.

As Guerrero et al also showed, the equation of state is the key to obtaining the direct correlation function in the mfa. They used the fact that the leading terms in the density expansions of the dcf's, $c_{\alpha\beta}(r)$,of the primitive version ($\alpha, \beta \in \{a, b\}$) are the Mayer f-functions:

$$c_{\alpha\beta}(r) = f_{\alpha\beta}(r) + \text{higher order terms} \tag{3}$$

and that the equation of state in the system is generally

$$\left(\frac{\partial \pi}{\partial \rho_\alpha}\right)_{\lambda_\beta} = 1 - \rho_a \int d\underline{r}\, c_{a\alpha}(r) - \rho_b \int d\underline{r}\, c_{\alpha\beta}(r) \tag{4}$$

to conclude that $c_{aa}(r) = c_{bb}(r) = 0,\ c_{ab}(\cancel{r}) = c_{ba}(r) = f_{ab}(r)$ They were then able to use a transcription argument to obtain the dcf in a homogeneous phase,

$$c(r) = \frac{\rho_b}{v_0} \int d\underline{r}_3\, f_{ba}(r_{13})\, f_{ab}(r_{32}) \tag{5}$$

The definition of this function is

$$h(r_{12}) = c(r_{12}) + \rho \int d\underline{r}_3\, h(r_{13})\, c(r_{32}) \tag{6}$$

and its inhomogeneous generalization by

$$h(\underline{r}_1, \underline{r}_2) = c(\underline{r}_1, \underline{r}_2) + \int d\underline{r}_3\, \rho(\underline{r}_3)\, h(\underline{r}_1, \underline{r}_3)\, c(\underline{r}_3, \underline{r}_2) \tag{7}$$

By direct analogy, Leng, Rowlinson and Thompson generalized (5):

$$c(\underline{r}_1, \underline{r}_2) = \frac{1}{v_0} \int d\underline{r}_3\, \rho_b(\underline{r}_3)\, f_{ba}(r_{13})\, f_{ab}(r_{32}) \tag{8}$$

which is identical to (5.7), the f-function being obtained from (5.1) and a function only of scalar separation.

Leng et al. (1976) had already introduced a mean-field approximation in a system with a planar interface, allowing molecules to take up a random configuration over planes parallel to the interface, to derive an equation for the density profile, (6.11),

$$\ln\left(\frac{\rho(-z)}{\lambda_a}\right) = -\frac{3}{4}\int_{-1}^{1} du\, \rho_a(z+u)\,(1-u^2) \qquad (9)$$

before they obtained (8). To demonstrate the equivalence of the two approaches they showed that (8) led to (9) when the Lovett-Mou-Buff-Wertheim integrodifferential equation, (9.1), for the density profile was used,

$$\underset{\sim}{\nabla}_1 \ln \rho(\underline{r}_1) = \frac{3}{4\pi}\int d\underline{r}_2\, c(\underline{r}_1, \underline{r}_2)\, \underset{\sim}{\nabla}_2 \rho(\underline{r}_2)\,. \qquad (10)$$

(This equation is quite general and independent of any approximations). Their proof that the Kirkwood-Buff and Triezenberg-Zwanzig routes yield the same surface tension could now be used as a second demonstration of the equivalence of the two approaches to the mfa although at the time the general equivalence of the two routes had not been shown (Schofield, 1979).

In the present work an equation for the density profile of a drop , (8.10) and (8.11), has been derived by taking the assumption that penetrable-sphere molecules are distributed randomly over a set of concentric spherical surfaces. In addition however, as shown in the first half of Chapter 9, this equation can also be derived from the generalized expression for the direct correlation function, (8) in conjunction with (10), a result completely analogous to that of Leng et al. (1977). Thus the equivalence of the two routes to the mfa is confirmed and the consistency of the use of (4.10) with the density profiles from (8.10) amd (8.11) ensured.

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