CENTENARY LECTURE *

Phase Equilibrium and Interfacial Structure

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1 Introduction

We shall discuss the equilibrium of fluid phases and the properties of the interfaces between them. We outline the theory that is current and see some of its successes, but the primary aim of this Lecture is to call attention to questions that are still unresolved.

Of particular (but not exclusive) concern are the critical points of those phase equilibria. We recall briefly in Part 2 how the properties of fluids and their interfaces vary near critical points; *i.e.*, what the critical indices (exponents) are. In Part 3 we describe the mean-field theory of inhomogeneous fluids, from which one obtains (approximately) the structure and thermodynamic properties of the interfaces between phases. Both these topics have been reviewed thoroughly and often,[1–5] but we set out in Parts 2 and 3 the major ideas and formulae we need to refer to later, so that this Lecture may be self-contained. It is then through a sequence of special topics, which we treat in the subsequent parts, that we see what some of the theory's successes and failures have been, what extensions of it are needed, and what some of the unsolved problems are.

2 Phase Equilibria and their Critical Points

In Figure 1*a* we see schematically the equilibrium between two phases α and β. This could be the equilibrium of a liquid β with its vapour α, or that between two incompletely miscible liquids. In Figure 1*b* is pictured the equilibrium of three phases, α, β, and γ, separated in pairs by two interfaces. Here β and γ may be two incompletely miscible liquids and α their common vapour, or all three may be liquids.

The critical points of phase equilibria are limiting states in which phases become identical and the interface between them disappears. In Figure 1*a* these may be the

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* Delivered at a Symposium of the Faraday Division of the Royal Society of Chemistry on 10 December, 1984 at Imperial College, London.

[1] J. S. Rowlinson and B. Widom, 'Molecular Theory of Capillarity' Oxford, 1982.

[2] D. Jasnow, *Rep. Prog. Phys.*, 1984, **47**, 1059.

[3] K. Binder, in 'Phase Transitions and Critical Phenomena', Vol. 8, ed. C. Domb and J. L. Lebowitz, Academic Press, 1983, pp. 1–144, 467–474.

[4] J. S. Rowlinson, *Chem. Soc. Rev.*, 1983, **12**, 251.

[5] B. Widom, *Faraday Symp. Chem. Soc.*, 1981, **16**, 7.

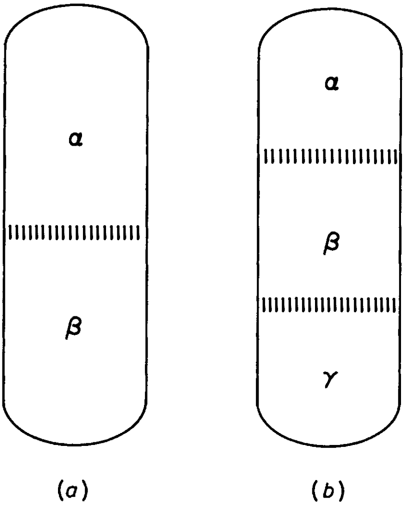

Figure 1

familiar critical points of liquid–vapour equilibrium or the consolute points of liquid–liquid equilibrium. In Figure 1*b*, the state in which the two phases β and γ become one at a critical point while the phase α remains in equilibrium with them but distinct, is called a critical endpoint; and there may similarly be a critical endpoint in which α and β become identical while in equilibrium with the distinct phase γ. The limiting state in which the two critical endpoints occur simultaneously, so that all three of α, β, and γ become one while both interfaces disappear, is called the tricritical point of the three-phase equilibrium.

When the interface between two phases disappears at a critical point the tension (free energy per unit area) of that interface vanishes, and does so proportionally to a positive power of the distance from the critical point. If we express this distance, as is most often done, as the difference $T_c - T$ between the temperature T of the phase equilibrium and the critical temperature T_c, then the surface (interfacial) tension σ behaves as

$$\sigma \sim \sigma_0(1 - T/T_c)^{\mu} \tag{1}$$

as $T \longrightarrow T_c$, where σ_0 and μ are positive parameters. We assume in (1) an 'upper' critical point, so that distinct phases exist for $T < T_c$. For a 'lower' critical point we replace $1 - T/T_c$ in (1) by $T/T_c - 1$.

For all ordinary critical points of two-phase equilibrium the exponent μ has the universal value $\mu = 1.26$ (as closely as we can tell from current theory and experiment[1]), but the coefficient σ_0 is not universal. By the scaling theory of critical points[1-3] σ is related to the coherence length ξ of density or composition fluctuations, and also to the difference $\Delta\rho$ in density or composition of the coexisting phases and to the compressibility (mechanical or osmotic) χ of the phases. Each of these also behaves as a power of $1 - T/T_c$ as the critical point is approached,

$$\xi \sim \xi_0(1 - T/T_c)^{-\nu} \tag{2}$$

$$\Delta\rho/\rho_c \sim B(1 - T/T_c)^{\beta} \tag{3}$$

$$\chi \sim \chi_0(1 - T/T_c)^{-\gamma} \tag{4}$$

(We must be careful not to confuse the exponents β and γ with the names of the phases β and γ.) Here ρ_c is the density or composition at the critical point; ν, β, and γ are universal exponents: $\nu = 0.63$, $\beta = 0.325$, $\gamma = 1.24$; while ξ_0, B, and χ_0 are non-universal amplitudes. We shall later see the scaling-theory connections of σ to ξ, $\Delta\rho$, and χ. These will then imply relations among the universal exponents μ, ν, β, and γ, as well as universal relations[6,7] among the otherwise non-universal amplitudes σ_0, ξ_0, B, and χ_0, and we shall examine these to see how well they hold in theoretical models and in experiment.

A critical endpoint is an ordinary critical point. At an $\alpha\beta$ critical endpoint in the system in Figure 1*b*, for example, the γ phase is merely a spectator to the $\alpha\beta$ critical point and has no more effect on it than does the container, which is indeed yet another phase. Thus, (1)—(4) and the scaling relations among those quantities all continue to hold for the critical phases (but not for the spectator phase) at a critical endpoint, and they do so with the values of the exponents already quoted. A tricritical point, which, as we noted, is the coincidence of two critical endpoints and is a limit of three-phase coexistence (in contrast to an ordinary critical point or critical endpoint, which is a limit of two-phase coexistence), is different. While the relevant σ, ξ, $\Delta\rho$, and χ near a tricritical point are again as in (1)—(4) (with T_c now the tricritical-point temperature), with exponents that are again universal, the values of the latter differ from those at an ordinary critical point: for tricritical points[1] $\mu = 2$, $\nu = 1$, $\beta = 1/2$, $\gamma = 2$.

We shall need to recall all this later, but for now we change the subject and outline the mean-field theory of inhomogeneous fluids.

3 Mean-field Theory

The structure and tension of interfaces may in principle be calculated from statistical mechanics once the intermolecular forces are known; but in practice this is done only approximately, most often with the van der Waals theory or one or another of its immediate extensions, which, collectively, are called the mean-field theory (or approximation).[1-3]

We shall see the theory here in its simplest context, that of liquid–vapour equilibrium across a planar interface in a one-component fluid. We think of the molecules as attracting hard spheres of diameter b. The potential energy of attraction as a function of the distance r between centres is $\varphi(r)$, with the convention $\varphi(\infty) = 0$. With z the distance perpendicular to and through the interface, the

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[6] D. Stauffer, M. Ferer, and M. Wortis, *Phys. Rev. Lett.*, 1972, **29**, 345.

[7] D. Stauffer, *Phys. Lett. A*, 1973, **44**, 261.

density ρ is z-dependent, $\rho = \rho(z)$, as in Figure 2, varying from the bulk gas-phase density $\rho(-\infty) = \rho_g$ to the bulk liquid-phase density $\rho(\infty) = \rho_l$ as z varies from $-\infty$ to ∞.

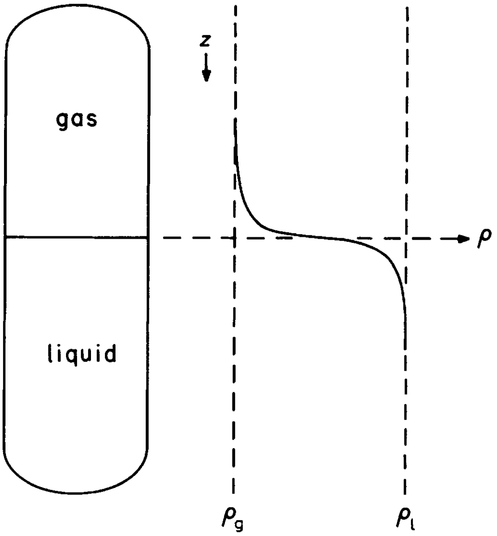

Figure 2

If we ignore correlations in the positions of the molecules other than the hard-sphere exclusions, the mean potential energy of attraction at any point P at depth z is

$$\int_{r>b} \varphi(r)\rho(z')d\tau,$$

where $d\tau$ is an element of volume at a variable point, z' is the depth at that point, r is the distance between that point and the point P, and the integration is over all such points outside a sphere of radius b about P (Figure 3). The mean-field approximation takes this potential energy to be the contribution the attractive forces make to the chemical potential of the fluid; there is imagined to be no entropic component of that contribution. At the same time the hard-sphere repulsions are taken to contribute $\mu^{hs}[\rho(z)]$ to the chemical potential, where the function $\mu^{hs}(\rho)$ is the chemical potential of a fluid of the same hard spheres without attraction $[\varphi(r) \equiv 0]$ at a uniform density ρ and at the temperature of the model fluid with attractions. If we represent by μ [not to be confused with the exponent in (1)], with no superscript and no indicated argument, the uniform chemical potential of the two-phase fluid, then our approximation is

$$\mu = \mu^{hs}[\rho(z)] + \int_{r>b} \varphi(r)\rho(z')d\tau \tag{5}$$

The terms on the right-hand side of (5) are separately z-dependent but their sum is not. The contributions of the hard-sphere repulsions and of the attractions are

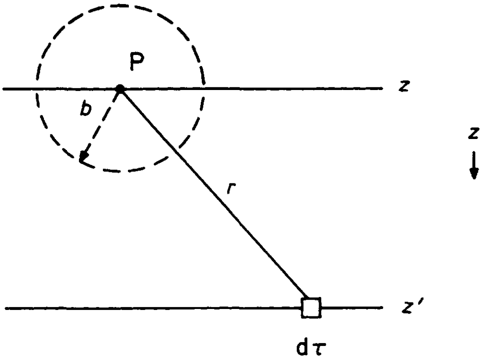

Figure 3

being taken to be separable (except for the hard-sphere exclusion in the range of integration) and additive. The former contribution is being taken to be local—$\mu^{\mathrm{hs}}(\rho)$ evaluated at the local $\rho(z)$—which is an approximation that would be accurate only if the density gradient $\mathrm{d}\rho(z)/\mathrm{d}z$ was so small that $\rho(z)$ was nearly constant over the distance b. The effect of the attractions is treated in (5) as fully non-local—molecules at all distances r from P for which $\varphi(r)$ is sensibly different from zero contribute to the potential at P—but is otherwise approximated as that of a mean field. Equation (5) is a functional equation for the density profile $\rho(z)$ in terms of the presumed known $\mu^{\mathrm{hs}}(\rho)$ and a given $\varphi(r)$.

If the fluid were (hypothetically) constrained to be uniform with the density ρ its chemical potential, $M(\rho)$, would by (5) be the analytic function

$$M(\rho) = \mu^{\mathrm{hs}}(\rho) - 2a\rho \tag{6}$$

in which a is van der Waals's a-parameter,

$$a = -\tfrac{1}{2}\int_{r>b} \varphi(r)\mathrm{d}\tau \tag{7}$$

In this mean-field theory the densities ρ_g and ρ_l of the bulk gas and liquid phases, at the chemical potential μ, satisfy

$$\mu = M(\rho_g) = M(\rho_l) \tag{8}$$

Also, in terms of this same function $M(\rho)$ defined by (6), the functional equation (5) is

$$\mu = M[\rho(z)] + \int_{r>b} \varphi(r)[\rho(z') - \rho(z)]\mathrm{d}\tau \tag{9}$$

The profile $\rho(z)$ is the solution of (5) or (9) that satisfies $\rho(-\infty) = \rho_g$ and $\rho(\infty) = \rho_l$ when ρ_g and ρ_l are solutions of (8).

When $\rho(z)$ is slowly varying (as it is near the critical point, where the interface is diffuse), (9) may be further approximated by expanding $\rho(z')$ about $z' = z$ and truncating after second order. Then

$$M[\rho(z)] - \mu = m\, \mathrm{d}^2\rho(z)/\mathrm{d}z^2 \tag{10}$$

where

$$m = -\tfrac{1}{6}\int_{r>b} r^2\varphi(r)\mathrm{d}\tau \tag{11}$$

[The coefficient of the first derivative, $\mathrm{d}\rho(z)/\mathrm{d}z$, vanishes by symmetry.] This is the simplest form of the van der Waals theory.$^{1-5}$ By analogy with the dynamics of a particle on a line, in which m plays the role of the mass, z that of the time, ρ that of the co-ordinate, and $M(\rho) - \mu$ that of the force, it is readily seen that the solution of (10) that satisfies $\rho(\pm\infty) = \rho_{g,l}$ when these, in turn, satisfy (8), is as in Figure 2.

The $\rho(z)$ determined by (9) may be seen by the methods of the variational calculus also to be that which minimizes a functional σ,

$$\sigma = \int_{-\infty}^{\infty}\{F[\rho(z)] + \tfrac{1}{4}\rho(z)\int_{r>b}\varphi(r)[\rho(z') - \rho(z)]\mathrm{d}\tau\}\mathrm{d}z \tag{12}$$

where the function $F(\rho)$ is defined in terms of $M(\rho) - \mu$ by

$$F(\rho) = \int_{\rho_g}^{\rho}[M(\rho) - \mu]\mathrm{d}\rho = -\int_{\rho}^{\rho_l}[M(\rho) - \mu]\mathrm{d}\rho \tag{13}$$

The second of (13) entails

$$\int_{\rho_g}^{\rho_l}[M(\rho) - \mu]\mathrm{d}\rho = 0 \tag{14}$$

This together with (8) amounts to Maxwell's equal-areas construction, which determines the ρ_g, ρ_l, and μ of the coexisting phases once the temperature is specified.

The integrand in the z-integration in (12) is the mean-field theory's approximation to the excess free-energy density due to the inhomogeneity, *i.e.*, arising from the z-dependence of ρ. Then σ, the integral over z, is the excess free energy per unit area, which is the interfacial tension; and the equilibrium profile $\rho(z)$ is then that which minimizes the tension.

This identification of the minimal σ in (12) with the equilibrium surface tension is confirmed by noting that it satisfies the condition, required by the Gibbs adsorption equation, that $\mathrm{d}(\sigma/T)/\mathrm{d}(1/T)$ be the excess surface energy per unit area when the Gibbs dividing surface is that of vanishing adsorption. Since the minimal σ is extremal with respect to variation of $\rho(z)$, in differentiating it with respect to T we need consider only the explicit temperature dependence of the integrand in (12) at fixed $\rho(z)$ and not the implicit dependence arising from the T-dependence of the equilibrium $\rho(z)$ itself. Furthermore, $[\mu^{hs}(\rho) - \mu]/T$ may be expressed as the difference between a function of ρ alone, independent of T, and a function of T alone, independent of ρ. With these two observations we have from (6)—(8) and (12)—(14),

$$\mathrm{d}(\sigma/T)/\mathrm{d}(1/T) = \tfrac{1}{2}\int_{-\infty}^{\infty}\int\varphi(r)[\rho_l\rho_g - (\rho_l + \rho_g)\rho(z) + \rho(z)\rho(z')]\mathrm{d}\tau\, \mathrm{d}z \tag{15}$$

If we define a function $\rho_{gl}(z)$ to be ρ_g when z is on the gas side of a dividing surface and ρ_l when z is on the liquid side, then the location of the dividing surface of vanishing adsorption is determined by

$$\int_{-\infty}^{\infty}[\rho(z) - \rho_{gl}(z)]\mathrm{d}z = 0 \tag{16}$$

There is no reference in (15) to any dividing surface; but if we now specify (16) then (15) becomes

$$\mathrm{d}(\sigma/T)/\mathrm{d}(1/T) = \tfrac{1}{2}\int_{-\infty}^{\infty}\int\varphi(r)[\rho(z)\rho(z') - \rho_{gl}(z)^2]\mathrm{d}\tau\,\mathrm{d}z \tag{17}$$

which is manifestly the excess surface energy per unit area in mean-field approximation.

In the same square-gradient approximation that led to (10), and after integration by parts converts $-\rho(z)\mathrm{d}^2\rho(z)/\mathrm{d}z^2$ to $[\mathrm{d}\rho(z)/\mathrm{d}z]^2$, the functional σ in (12) becomes

$$\sigma = \int_{-\infty}^{\infty}\{F[\rho(z)] + \tfrac{1}{2}m[\mathrm{d}\rho(z)/dz]^2\}\mathrm{d}z \tag{18}$$

This is the 'action' in the dynamical analogy; the equilibrium σ may then be equally well expressed as the integral of the 'momentum' over the 'co-ordinate',

$$\sigma = \sqrt{2m}\int_{\rho_g}^{\rho_l}\sqrt{F(\rho)}\,\mathrm{d}\rho \tag{19}$$

In much of the current work on inhomogeneous fluids (5), (9), or (12) (they are equivalent), or some direct extension of them, is the starting point. They are immediately generalizable to potentials that include external fields, to multi-component systems, and to inhomogeneities that are more than one-dimensional, where the densities depend on two or all three spatial co-ordinates. An important example of a two-dimensional inhomogeneity is the line in which three phases meet, where the several densities (in a multi-component system) depend on the two co-ordinates in any plane perpendicular to that line.[1]

While the generalizations to include external fields, to multi-component systems, and to multi-dimensional inhomogeneities are straightforward, other generalizations are not, and may call for correction to the basic mean-field idea. Even then this remains a useful theoretical framework. In the remaining parts of this Lecture, as we treat a succession of problems and call attention to some unanswered questions, we refer repeatedly to these ideas and formulae, as well as to those in Part 2 relating to critical points.

4 Surface Tension Near Critical Points

We may use the theory of the preceding section to discuss further the critical-point behaviour of surface tension, which we outlined in Part 2. Near the critical point the interface is diffuse and the density or composition gradients are small, so for many purposes the version of the theory in (18) and (19) is adequate.

When $\rho(z)$ is the equilibrium profile the two terms $\int F\mathrm{d}z$ and $\frac{1}{2}m\int(\mathrm{d}\rho/\mathrm{d}z)^2\mathrm{d}z$ in (18) contribute equally to σ. Furthermore, on comparing this theory of interfacial structure with the Ornstein–Zernike theory of density or composition fluctuations near critical points,[1] one sees that the distance through the interface over which the variation of the composition from that of one bulk phase to that of the other mainly occurs—hence, the interfacial thickness, or the range of z over which the integrand in (18) differs sensibly from 0—is the same as the coherence (correlation) length ξ of the fluctuations in the bulk phases, to which we referred in Part 2. Then from (18) we estimate $\sigma \sim Km(\Delta\rho)^2/\xi$, where K is some dimensionless proportionality constant and where $\Delta\rho$ ($= \rho_l - \rho_g$ for a liquid–vapour interface) is just the density or composition difference referred to in Part 2. From the Ornstein–Zernike theory of fluctuations one knows that near the critical point

$$\xi \sim \rho_c \sqrt{m\chi} \tag{20}$$

with χ the compressibility, as in Part 2. Thus,

$$\sigma \sim K\xi\,(\Delta\rho/\rho_c)^2\chi^{-1} \tag{21}$$

Here ξ and χ may be evaluated in either bulk phase; near the critical point ξ is the same in the two phases, as is χ.

If we take the mean-field theory literally we may evaluate $\Delta\rho/\rho_c$ and χ from (6)—(8) and (14) [and the thermodynamic identity $\chi^{-1} = \rho^2(\partial\mu/\partial\rho)_T$], m from (11), ξ from (20), and σ from (6), (13), and (19). We find (1)—(4) to hold with the classical values $\mu = 3/2$, $\nu = 1/2$, $\beta = 1/2$, and $\gamma = 1$ of the exponents; we find explicit values of the coefficients σ_0, ξ_0, B, and χ_0; and for the dimensionless coefficient K in (21), which is related to the coefficients in (1)—(4) by

$$K = \sigma_0\chi_0/B^2\xi_0, \tag{22}$$

we find the explicit and universal value $K = 1/6$.

These values of the exponents μ, ν, β, and γ are not those quoted in Part 2; the mean-field theory does not give a quantitatively correct account of critical-point behaviour. We may reasonably suppose that if in (18) or (19) we used a function $F(\rho)$ that we knew contained the right critical-point singularities, instead of that obtained from (6) *via* (13), we would get the right answers. [We would also need to replace the potential $\varphi(r)$ in (11) by $-kT$ times the direct correlation function $c(r)$ to obtain m correctly; k is Boltzmann's constant. It is with this m, more generally, that the interfacial thickness ξ, or the correlation length ξ of the Ornstein–Zernike theory, is related to χ by (20).] The result is again of the form (21), but now with non-classical values of the exponents μ, ν, β, and γ, and with a generally different but again universal value of K related to the non-universal amplitudes σ_0, χ_0, B, and ξ_0 by (22). From (21) we find the relation

$$\mu = -\nu + \gamma + 2\beta \tag{23}$$

among these four exponents, which we may verify holds with the values of the exponents quoted earlier.

Fluctuation theory gives $\overline{(\delta\rho)^2} = \rho^2 kT\chi/v$ for the density fluctuations $\delta\rho$ in a macroscopic sub-volume v of a fluid. By critical-point scaling theory the fluctuations in density in a volume ξ^d (d = dimensionality) in either of two coexisting, near-critical phases are of the order of the difference, $\Delta\rho$, of the densities of those phases. Thus, $(\Delta\rho/\rho_c)^2 \sim K'kT_c\,\chi/\xi^d$ with some universal proportionality constant K'. Also by the scaling theory the free energy associated with the elementary, coherent density fluctuation of coherence length ξ is kT; while the magnitude of the typical density fluctuation in the volume ξ^d is $\Delta\rho$, so the free energy associated with it is at the same time of order $\sigma\xi^{d-1}$. Hence, $\sigma\xi^{d-1} \sim K''kT_c$, with still another universal proportionality constant K''. These give us the further exponent relations

$$d\nu = \gamma + 2\beta, \quad \mu = (d-1)\nu \tag{24}$$

which are consistent with (23), and the further universal relations among non-universal amplitudes,

$$K' = B^2\xi_0^d/kT_c\chi_0, \quad K'' = \sigma_0\xi_0^{d-1}/kT_c, \tag{25}$$

which are consistent with (22) with $K = K''/K'$. The relations (24) with $d = 3$ may also be verified to hold with the quoted values of the exponents, which is an important success of the theory; but there is an as yet unresolved discrepancy between theory and experiment with respect to the universal relations among amplitudes that include σ_0; *i.e.*, in the values of K and K''. Careful analyses of the experimental results[8–10] reveal that $\sigma_0\chi_0/B^2\xi_0$ and $\sigma_0\xi_0^{d-1}/kT_c$ are indeed universal, but that their universal values are about twice as great as the theoretical estimates of these quantities[11–13] in models whose critical properties have been thought to be identical with those of real fluids. The discrepancy is believed[9] to reside in σ_0. Until it is resolved the present theory of surface tension near critical points cannot be accepted as final.

We saw in Part 2 that the critical-point exponent for the vanishing of the interfacial tensions at a tricritical point is supposed theoretically to be $\mu = 2$, rather than $\mu = 1.26$ as at an ordinary critical point of two-phase equilibrium. Together with the other values of the tricritical-point exponents quoted in Part 2, the value $\mu = 2$ satisfies (23), and also (24) with $d = 3$. There has been no experimental determination of the exponent μ for a tricritical point of ordinary three-phase equilibrium, so this theoretical prediction remains untested, except indirectly: the

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[8] M. B. Schneider, personal communication (1984).

[9] M. R. Moldover, *Phys. Rev. A*, 1985, **31**, 1022.

[10] H. L. Gielen, O. B. Verbeke, and J. Thoen, *J. Chem. Phys.*, 1984, **81**, 6154.

[11] K. Binder, *Phys. Rev. A*, 1982, **25**, 1699.

[12] E. Brezin and S. Feng, *Phys. Rev. B*, 1984, **29**, 472.

[13] K. K. Mon and D. Jasnow, *Phys. Rev. A*, 1984, **30**, 670.

equilibrium between the superfluid and non-superfluid liquid phases of ^{3}He–^{4}He mixtures is believed to be thermodynamically equivalent to three-phase equilibrium in classical fluids[14,15] (we shall say more about this for pure ^{4}He in Part 5); and measurements of the interfacial tension near the liquid–liquid consolute point of those mixtures[16] are consistent with $\mu = 2$.

In the phase equilibria of microemulsions one often finds a microemulsion, containing large amounts of both oil and water (or brine) in a homogeneous solution with a surfactant, in equilibrium with a phase that is almost pure oil, or one that is almost pure water (or brine)—or with both, in a three-phase equilibrium. The composition of the microemulsion is far from that of the phase or phases with which it is in equilibrium, so in that sense one is far from a critical point; yet the interfacial tensions are extraordinarily low[17–19] (10^{-2}—10^{-3} dyne cm^{-1}), as when near a critical point in systems without surfactant. We may understand that[20] from the theory in Part 3. From (19),

$$\sigma \cong (2m\bar{F})^{\frac{1}{2}}\,\Delta\rho \qquad (26)$$

where $\bar{F}$ is a typical value of F in the interface, or even, for order-of-magnitude estimates, the maximum value. Here ρ is any measure of chemical composition while $F(\rho)$, from (6) and (13), is as in Figure 4, with ρ_α and ρ_β the values of ρ in the bulk phases. Near a critical point $\bar{F}^{\frac{1}{2}}$ and $\Delta\rho$ are both small. In the microemulsion phase equilibria that we are contemplating $\Delta\rho$ is not small, but $F(\rho)$ is nevertheless extremely small[21] over the whole interval $\rho_\alpha \leq \rho \leq \rho_\beta$; so $\bar{F}^{\frac{1}{2}}$ is small, and thence also σ.

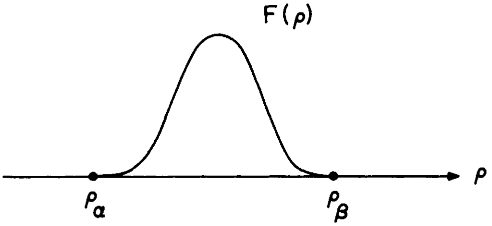

Figure 4

5 Non-critical Interfaces Near Critical Endpoints

Let us imagine in Figure 1*b* that α is the vapour in equilibrium with two liquids β and γ that are near their consolute point; or that α is a wall, or a solid adsorbent, while β and γ are the liquid and vapour phases of a fluid near its critical point or

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[14] R. B. Griffiths, *Phys. Rev. Lett.*, 1970, **24**, 715.

[15] R. B. Griffiths, *Phys. Rev. B*, 1973, **7**, 545.

[16] P. Leiderer, H. Poisel, and M. Wanner, *J. Low Temp. Phys.*, 1977, **28**, 167.

[17] A. M. Bellocq, D. Bourbon, and B. Lemanceau, *J. Disp. Sci. Tech.*, 1981, **2**, 27.

[18] A. Pouchelon, D. Chatenay, J. Meunier, and D. Langevin, *J. Coll. Interf. Sci.*, 1981, **82**, 418.

[19] A. M. Cazabat, D. Langevin, J. Meunier, and A. Pouchelon, *Adv. Coll. Interf. Sci.*, 1982, **16**, 175.

[20] H. T. Davis and L. E. Scriven, presented at the 55th Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of the AIME, Dallas, Sept. 21—24, 1980.

[21] Y. Talmon and S. Prager, *Nature*, 1977, **267**, 333.

again two liquid phases near a consolute point. In each case α is the spectator phase at the βγ critical point (critical endpoint; Part 2). The βγ interface is the one we discussed in Part 4, but here we concentrate on the non-critical αβ or αγ interfaces, and we ask, in particular, how the βγ critical point manifests itself in the tensions of those interfaces.

We may again use the theoretical framework of Part 3, now with $F(\rho)$ as in Figure 5, or even an explicitly two-density version of the theory for the two-component liquid mixture.[22,23] The results[1,22,23] are as in Figure 6. Here $\sigma_{\alpha,\beta\gamma}$ is the tension of the interface between the spectator phase α and the single βγ phase above the βγ critical point at the critical density or composition, while $\sigma_{\alpha\beta}$ and $\sigma_{\alpha\gamma}$ are the separate tensions of the αβ and αγ interfaces in the three-phase region below the βγ critical point. The latter tensions are related to each other and to the tension $\sigma_{\beta\gamma}$ of the critical interface by

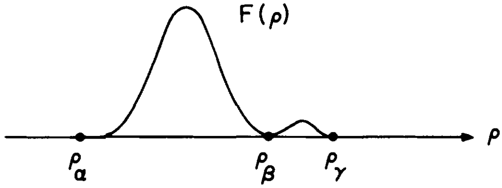

Figure 5

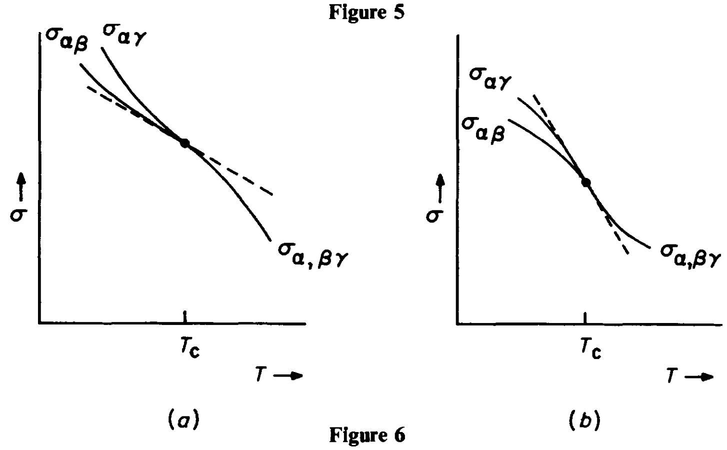

Figure 6

$$\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma} \qquad (27)$$

(Antonow's rule[1]), as follows from Figure 5 and equation 19 (with 'ρ_g' and 'ρ_l' taken to be ρ_α, ρ_β, or ρ_γ, as appropriate).

Figure 6*a* is found when the βγ critical point is incorporated in $F(\rho)$ with classical

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[22] M. M. Telo da Gama, R. Evans, and I. Hadjiagapiou, *Mol. Phys.*, 1984, **52**, 573.
[23] M. E. Costas, C. Varea, and A. Robledo, *Phys. Rev. Lett.*, 1983, **51**, 2394.

(mean-field-theory) exponents and Figure 6*b* when the exponents are non-classical. In each of the figures all three curves, $\sigma_{\alpha\beta}$, $\sigma_{\alpha\gamma}$, and $\sigma_{\alpha,\beta\gamma}$, are of the form

$$\sigma \sim \sigma_c - A(T - T_c) + C|T - T_c|^{\mu} \tag{28}$$

in the immediate neighbourhood of the critical point, where μ, as before, is the exponent in the critical surface tension $\sigma_{\beta\gamma}$ (so $\mu = 3/2$ or 1.26 in the classical and non-classical versions of the theory, respectively), and A is a common constant for all three curves, which are thus predicted to share a common tangent (the dashed line in each figure), while C is a different constant for each curve and of opposite sign on the two sides of the critical point. Thus, the deviations of the curves from their common tangent is predicted to be of one sign on one side of the critical point and of opposite sign on the other, as shown in the figures. This last feature, which appears as an inevitable and universal consequence of the theory, is not (or has not yet been) verified by experiment. There is an indication from theory[1] that in Figure 6*b* the curve $\sigma_{\alpha\gamma}$ may quickly turn upward on departing from the critical point and mostly lie above the tangent except very near the critical point itself. That could greatly complicate the interpretation of experiment. The experiments[24,25] have not yet been of sufficient precision to resolve these questions, but, disquietingly, in some cases all three curves seem to lie above their tangent. We shall shortly pose a related question about the surface tension of liquid helium near its lambda point.

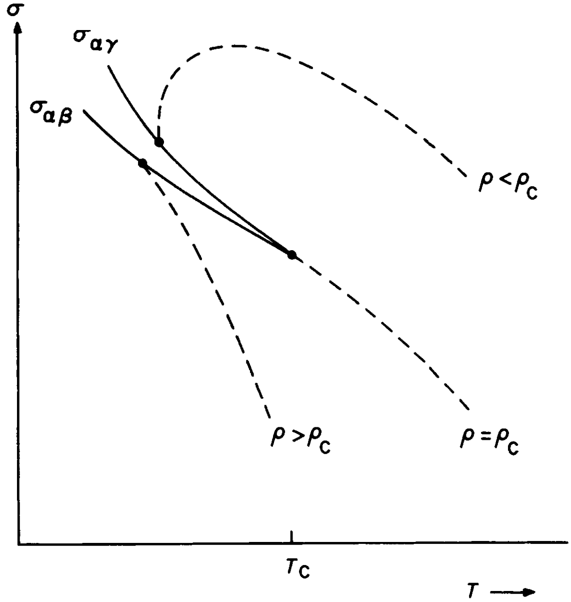

Figure 7

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[24] N. Nagarajan, W. W. Webb, and B. Widom, *J. Chem. Phys.*, 1982, 77, 5771.

[25] I. L. Pegg and I. McLure: I. L. Pegg, Ph.D. thesis, University of Sheffield, 1982.

Another prediction of theory that experiment has so far been too imprecise to test is the difference in the way curves of $\sigma_{\alpha,\beta\gamma}$ *vs.* T at fixed non-critical composition or density come in to the boundary of the three-phase region according to whether the fixed composition is on one side or the other of critical. In Figure 7 we see again the curves $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta}$ of Figure 6*a*, and also the curve there called $\sigma_{\alpha,\beta\gamma}$, now drawn dashed and labelled $\rho = \rho_c$. The other dashed curves are also the tensions of the $\alpha,\beta\gamma$ interface in the two-phase region as functions of temperature, each now at a fixed, off-critical composition or density.

Because of (27), when all three phases are in equilibrium the phase β wets perfectly, or spreads at, the $\alpha\gamma$ interface. Then when $\beta\gamma$ is still a single, homogeneous phase in equilibrium with α, with a fixed composition on the γ side of critical ($\rho < \rho_c$, say, as in Figure 7), as T decreases and the phase-separation point is approached a premonitory layer of β forms at the interface with α and gradually logarithmically slowly—grows to macroscopic thickness as β comes ever closer to being stable in bulk.[1–3,5,26–29] In the limit there is then an infinite adsorption at the $\alpha\gamma$ interface, and so, according to the Gibbs adsorption equation, a (logarithmic) divergence in $(\partial\sigma/\partial\mu)_T = -(\partial\rho/\partial\mu)_T(\partial T/\partial\rho)_\sigma(\partial\sigma/\partial T)_\rho$ (now μ is again chemical potential, not the surface-tension exponent), and so also in $(\partial\sigma/\partial T)_\rho$, since away from the critical point the other two factors are both finite. Thus, the dashed curve marked $\rho < \rho_c$ in Figure 7 comes into the limiting curve $\sigma_{\alpha\gamma}$ with infinite slope,[26] as shown. On the β side of critical no premonitory layer of γ forms at the interface with α because the $\alpha\beta$ interface is not wet by γ, so the curve marked $\rho > \rho_c$ in Figure 7 comes into the limiting curve $\sigma_{\alpha\beta}$ with finite slope, as also shown. Direct measurements[24] of $\sigma_{\alpha,\beta\gamma}$ have so far failed to reveal the predicted divergence of the slopes of the curves $\rho < \rho_c$.

The phenomenon we just discussed is not specifically connected to the critical point. On the contrary, as we see in Figure 7, the amplitude of the predicted singularity becomes smaller as the critical point is approached: the curve of $\sigma_{\alpha,\beta\gamma}$ *vs.* T at $\rho = \rho_c$ shares a common tangent there with the curve $\sigma_{\alpha\gamma}$ *vs.* T, as in Figure 6. On the other hand, when too far from the critical point we may be in a regime[26] in which $\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ instead of (27); then β no longer wets the $\alpha\gamma$ interface, a premonitory β layer is no longer formed, and we would no longer expect the curves $\rho < \rho_c$ (Figure 7) to be of infinite slope where they meet the curve $\sigma_{\alpha\gamma}$.

Measurements of the adsorption—in effect, direct measurements of the derivatives of σ—would probe such singularities more sensitively than do measurements of σ itself. Adsorption measurements[30–33] have been called on to

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[26] J. W. Cahn, *J. Chem. Phys.*, 1977, **66**, 3667.

[27] R. Pandit, M. Schick, and M. Wortis, *Phys. Rev. B*, 1982, **26**, 5112.

[28] H. Nakanishi and M. E. Fisher, *Phys. Rev. Lett.*, 1982, **49**, 1565.

[29] A. Robledo, 'Las Transiciones Interfaciales', preprint (1984).

[30] (*a*) D. Beaglehole, *J. Chem. Phys.*, 1980, **73**, 3366; *Phys. Lett. A*, 1982, **91**, 237; (*b*) A. V. Mikhailov, V. L. Kuz'min, and A. I. Rusanov, *Kolloid. Zhur.*, 1984, **46**, 481.

[31] B. Heidel and G. H. Findenegg, *J. Phys. Chem.*, 1984, **88**, 6575.

[32] J. Specovius and G. H. Findenegg, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, 690; S. Blümel and G. H. Findenegg, *Phys. Rev. Lett.*, 1985, **54**, 447.

[33] G. H. Findenegg and R. Löring, *J. Chem. Phys.*, 1984, **81**, 3270; R. Loring and G. H. Findenegg, *J. Coll. Interf. Sci.*, 1981, **84**, 355.

test another prediction of theory, this one concerned more specifically with behaviour near the critical point. If we follow $\sigma_{\alpha,\beta\gamma}$ as a function of $\Delta\rho$ at $T = T_c$ we find,[1] as the counterpart of (28),

$$\sigma_{\alpha,\beta\gamma} \sim \sigma_c + D_{\pm}|\Delta\rho|^{\mu/\beta} \tag{29}$$

with μ and β the critical-point exponents already defined and with $D_{\pm}$ two different constants according as $\Delta\rho > 0$ or $\Delta\rho < 0$. The singular terms $|T - T_c|^{\mu}$ in (28) and $|\Delta\rho|^{\mu/\beta}$ in (29) are equivalent to each other *via* critical-point scaling [*cf.* equation 3], but refer to two different paths of approach to the critical point: the first to the path $\rho = \rho_c$ with T varying and the second to the path $T = T_c$ with ρ varying. Then the adsorption $\Gamma = (\partial\sigma/\partial\mu)_T = (\partial\sigma/\partial\rho)_T\, \rho^2\chi$ [from the identity $\chi^{-1} = \rho^2(\partial\mu/\partial\rho)_T$ we referred to in Part 4] at the $\alpha,\beta\gamma$ interface behaves as $\Gamma \sim |\Delta\rho|^{(\mu-\beta-\gamma)/\beta}$ along the critical isotherm ($T = T_c$), from (29), (3), and (4); and thus, again by critical-point scaling, $\Gamma \sim |T - T_c|^{\mu-\beta-\gamma}$ on the path $\rho = \rho_c$. By (23) this is

$$\Gamma \sim |T - T_c|^{-(\nu-\beta)} = |T - T_c|^{-0.3} \tag{30}$$

a result first obtained by Fisher and de Gennes.[34]

Here, too, experiment and theory are not yet in perfect accord: with β and γ (or $\beta\gamma$) the liquid phases of aniline–cyclohexane mixtures and with α their vapour, Beaglehole[30a] found an exponent close to 0, more nearly consistent with a logarithmic divergence than with $|T - T_c|^{-0.3}$, while in analogous systems Mikhailov *et al.*[30b] found the exponent 0.35 ± 0.15; with β and γ (or $\beta\gamma$) the fluid phases of pure ethylene, and with graphite as the α phase, Specovius and Findenegg[32] did indeed find the exponent −0.3; but these have been superseded by the more accurate measurements of Blümel and Findenegg[32] with SF_6 in place of ethylene, and the result is an exponent closer to −0.5. For propane on two forms of graphite the exponents that are found are also in this range, −0.31 and −0.44 (Findenegg and Löring[33]). The theory may well be right, but it is not yet proved.

The surface tension of liquid helium near its lambda point T_λ falls in this class of phenomena, because that point is a critical point at which the superfluid order parameter ψ—the analogue of our earlier $\Delta\rho$—first appears; then, as T falls below T_λ, $|\psi|$ increases from 0, as in (3). There do not appear two spatially separated liquid phases β and γ, so there is no identifiable $\beta\gamma$ interface; also there are no separate $\alpha\beta$ and $\alpha\gamma$ interfaces: there is only one liquid–vapour interface below as well as above T_λ.

The appropriate theory[35] is one that recognizes explicitly both the density ρ, which differentiates liquid and vapour, and the superfluid order parameter ψ, and is thus a two-component (or multi-component, depending on the dimensionality of ψ) generalization of the theory outlined in Part 3. The result is again as in (28). The helium lambda point is not exactly of the class of ordinary, two-phase critical points, so the value of the exponent μ is slightly different from 1.26—now closer to 1.35—but that is a minor difference. The mean-field theory[35] of this liquid–vapour

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[34] M. E. Fisher and P. G. de Gennes, *C. R. Hebd. Seances Acad. Sci., Ser. B*, 1978, **287**, 207.

[35] P. Tavan and B. Widom, *Phys. Rev. B*, 1983, **27**, 180.

interface again gives $\mu = 3/2$, but it gives a coefficient C in (28) that is non-zero only for $T < T_\lambda$; above T_λ there are only integer powers of $T - T_\lambda$ in σ. This is as in an earlier theory by Sobyanin,[36] but Hohenberg[37] has argued that the singular term $|T - T_\lambda|^\mu$ should appear in σ on both sides of the λ-point. The question is still unresolved theoretically. Experimentally,[38] it appears that the singular term is present on both sides, and that the data are well fit with the power $\mu = 1.35$.

Both by theory[35] and experiment[38] the curve σ *vs.* T lies entirely above the line that is tangent to it at $T = T_\lambda$, as shown schematically in Figure 8. This differs from the result in Figure 6. There we distinguished two curves, $\sigma_{\alpha\beta}$ and $\sigma_{\alpha\gamma}$, for $T < T_c$, while here for $T < T_\lambda$ there is only one, but that does not account for the difference, which is still not clearly understood. The difference is not due only to there being here two densities, ρ and ψ, instead of one, for some of the calculations for the ordinary critical endpoint were also based on two-density versions of the theory.[22] What may be the significant difference between the former and present problems is that in helium the vapour phase is symmetrically related to the superfluid 'phases' below T_λ while at an ordinary critical endpoint the distinct phase is unsymmetrically related to the two near-critical phases; but if this is the explanation it has yet to be convincingly demonstrated.

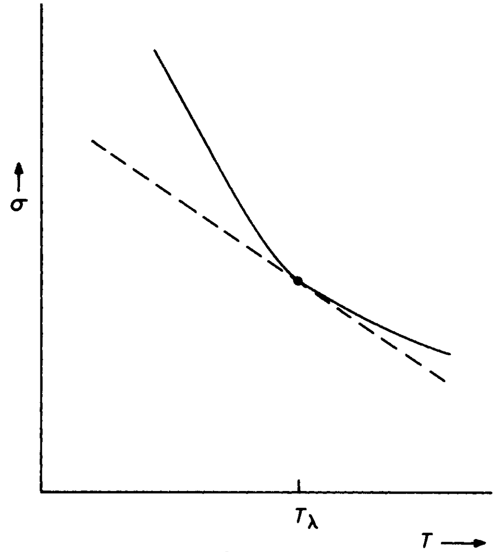

Figure 8

6 Long-range Forces

Does it matter very much in the theory based on (9) or (12) whether the intermolecular potential $\varphi(r)$ vanishes proportionally to $1/r^6$, say, at large r, or is

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[36] A. A. Sobyanin, *Sov. Phys. JETP*, 1972, **34**, 229.

[37] P. C. Hohenberg, *J. Low Temp. Phys.*, 1973, **13**, 433.

[38] J. H. Magerlein and T. M. Sanders, Jr., *Phys. Rev. Lett.*, 1976, **36**, 258.

much shorter ranged than that? There have been some surprising answers.

According to the mean-field theory it is only in an inhomogeneous system that it could matter. In a homogeneous fluid the theory reduces simply to the equation of state

$$\mu = \mu^{hs}(\rho) - 2a\rho \tag{31}$$

[*cf.* equation 6] with a given by (7). Thus, any two $\varphi(r)$ that have the same integral outside hard cores of equal diameter b lead to the same equation of state; whether φ is long-ranged or short-ranged is irrelevant, as long as it is integrable.

Even in an inhomogeneous system, if the square-gradient approximation (10) or (18) were sufficient, long-rangedness of $\varphi(r)$ would again have no effect, provided only that φ were not so long-ranged that its second moment m failed to exist (equation 11); *i.e.*, provided that $\varphi(r)$ vanished faster than $1/r^5$ (as $1/r^6$, for example) as $r \longrightarrow \infty$. Then any two fluids in which the molecules had the same core diameter b and attractive potentials with the same integral and same second moment would behave identically, however different the ranges of those potentials.

For an ordinary interface between two bulk phases, such as that whose profile is shown schematically in Figure 2, even when it is necessary for quantitative accuracy to go beyond the square-gradient approximation, neither the profile nor the tension is markedly affected by the range of φ as long as a and m are fixed.[39,40] To be sure, the rapidity of approach of $\rho(z)$ to ρ_g or ρ_l as $|z| \longrightarrow \infty$ does depend on the range of φ. When $\varphi(r)$ is of strictly finite range [*i.e.*, when $\varphi(r) \equiv 0$ for r greater than some fixed, microscopic distance], or when it vanishes exponentialy rapidly as $r \longrightarrow \infty$, then $\rho(z) - \rho_g$ or $\rho_l - \rho(z)$ vanishes exponentially rapidly as $|z| \longrightarrow \infty$, proportionally to $\exp(-|z|/\xi)$, with ξ the correlation length we encountered earlier, which, near the critical point, is related to the second moment of φ and to the compressibility χ by (20). When $\varphi(r)$, instead, vanishes proportionally to $-\varphi_0/r^n$ for large r, with some constant $\varphi_0 > 0$ and with $n > 3$,

$$|\rho(z) - \rho_{g,l}| \sim 2\pi\varphi_0(\rho_l - \rho_g)\,\rho_{g,l}^2\chi_{g,l}/(n-2)(n-3)|z|^{n-3} \tag{32}$$

as $|z| \longrightarrow \infty$, where g,l means either g or l consistently, and where $\rho_{g,l}$ and $\chi_{g,l}$ are the density and compressibility of the bulk phases. Thus, the decay is as $1/|z|^{n-3}$ instead of exponential; but if $n > 5$ (so that φ has a second moment), by the time the power-law decay is perceptibly different from the exponential, $\rho(z)$ is already so close to its asymptotic limit of ρ_g or ρ_l that the difference is of little consequence.

It is entirely different for a slab with two interfaces, as when in Part 5, for example, we dealt with a premonitory layer of a wetting phase β, let us say of thickness l, at an $\alpha\gamma$ interface (Figure 9). The importance of long-range forces in such geometries has been emphasized by de Gennes;[41] in particular, the range of the forces is found [42–57] to be crucial in determining the order of the 'wetting

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[39] J. A. Barker and J. R. Henderson, *J. Chem. Phys.*, 1982, **76**, 6303.

[40] B. Q. Lu, R. Evans, and M. M. Telo da Gama, preprint (1985).

[41] P. G. de Gennes, *J. Phys. (Paris), Lett.*, 1981, **42**, L-377.

transition',[26-29,58-60] which is a transition in the structure of the $\alpha\gamma$ interface between microscopic and macroscopic thicknesses l (Figure 9).

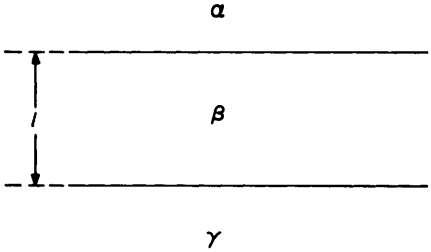

Figure 9

Tarazona *et al.*[42-44] have made the important remark that when (9) (or its generalization for multi-component systems) is applied to the configuration of Figure 9, and the equilibrium profiles $\rho(z)$ are found by solving (9) iteratively, the solution converges quickly, after only a few iterations, to its final form at the $\alpha\beta$ and $\beta\gamma$ faces of the β film, but only very slowly to the final equilibrium thickness l. This then allows one to separate the short-range and long-range aspects of the film structure, and to define an effective film free-energy per unit area, $\sigma(l)$, by first specifying an $F(\rho)$ suitable to the problem at hand and then substituting for $\rho(z)$ on the right-hand side of (12) a roughly correct form with variable thickness l. The equilibrium l is then that which minimizes $\sigma(l)$. In this way[42-44,59,60] problems such as that of the wetting transition are reduced to much simpler problems of one, or very few, degrees of freedom. It is related also (although it is more phenomenological and less microscopic) to the way one constructs an interface Hamiltonian,[61] which may again be a function $\sigma(l)$, or a functional $\sigma[l(x,y)]$ with x and y the co-ordinates in a plane parallel to the interfaces in Figure 9.

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[42] P. Tarazona and R. Evans, *Mol. Phys.*, 1983, **48**, 799.

[43] P. Tarazona, M. M. Telo da Gama, and R. Evans, *Mol. Phys.*, 1983, **49**, 283.

[44] P. Tarazona, M. M. Telo da Gama, and R. Evans, *Mol. Phys.*, 1983, **49**, 301.

[45] P. G. de Gennes, *C. R. Hebd. Seances Acad. Sci.*, (II), 1983, **297**, 9.

[46] E. H. Hauge and M. Schick, *Phys. Rev. B*, 1983, **27**, 4288.

[47] M. P. Nightingale, W. F. Saam, and M. Schick, *Phys. Rev. Lett.*, 1983, **51**, 1275.

[48] M. P. Nightingale, W. F. Saam, and M. Schick, *Phys. Rev. B*, 1984, **30**, 3830.

[49] R. Lipowsky and D. M. Kroll, *Phys. Rev. Lett.*, 1984, **52**, 2303; D. M. Kroll and T. F. Meister, *Phys. Rev. B*, 1985, **31**, 392.

[50] G. F. Teletzke, L. E. Scriven, and H. T. Davis, *J. Chem. Phys.*, 1982, **77**, 5794.

[51] G. F. Teletzke, L. E. Scriven, and H. T. Davis, *J. Chem. Phys.*, 1983, **78**, 1431.

[52] R. E. Benner, Jr., G. F. Teletzke, L. E. Scriven, and H. T. Davis, *J. Chem. Phys.*, 1984, **80**, 589.

[53] V. Privman, *J. Chem. Phys.*, 1984, **81**, 2463.

[54] M. P. Nightingale and J. O. Indekeu, *Phys. Rev. Lett.*, 1985, **54**, 1824.

[55] S. Dietrich, M. P. Nightingale, and M. Schick, preprint (1984).

[56] S. Dietrich and M. Schick, *Phys. Rev. B*, 1985, **31**, 4718.

[57] C. Ebner, W. F. Saam, and A. K. Sen, preprint (1984).

[58] D. E. Sullivan, *Faraday Symp. Chem. Soc.*, 1981, **16**, 191.

[59] D. E. Sullivan and M. M. Telo da Gama, in 'Fluid Interfacial Phenomena', ed. C. A. Croxton, Wiley, 1985.

[60] P. G. de Gennes, 'Wetting: Statics and Dynamics', preprint (1984).

[61] D. A. Huse, W. van Saarloos, and J. D. Weeks, preprint (1984).

We may illustrate this procedure by an example in which the β film of Figure 9 would not be quite stable as a bulk phase, there being some positive undersaturation-free-energy per unit volume, say f, which would vanish if the film were stable in bulk. We consider the example in which the mass density d_β of the wetting film is greater than the density d_γ of the γ phase,[62] which is itself of macroscopic thickness $H \gg l$ (Figure 10); then $f = (d_\beta - d_\gamma)gH$ with g the acceleration of gravity. For simplicity, and just as a schematic illustration of the method, let us assume a common $\varphi(r)$ for all the interactions and then take the number densities ρ_α, ρ_β, and ρ_γ to be such that ρ_β is the intermediate one, say $\rho_\alpha < \rho_\beta < \rho_\gamma$ (unlike the mass densities, which are in the order $d_\alpha < d_\gamma < d_\beta$). In this way the bulk phases are ordered α, γ, β in the gravitational field and yet the interfacial energetics are such as to favour the order α, β, γ. This leads to the configuration in Figure 10 with a microscopic but positive l, as we shall see.

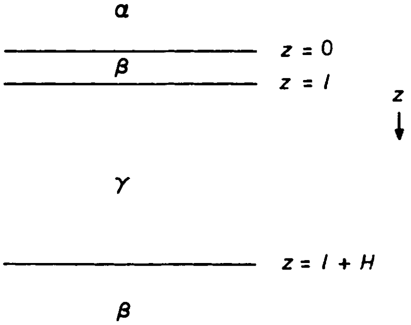

Figure 10

We now take (12) to be

$$\sigma(l) = fl + \tfrac{1}{2}\int_{-\infty}^{\infty}\int_{r>b}\varphi(r)[\rho(z') - \rho(z)]\rho(z)\mathrm{d}\tau\,\mathrm{d}z \tag{33}$$

with $\rho(z) = \rho_\alpha$ for $-\infty < z < 0$, $\rho(z) = \rho_\beta$ for $0 < z < l$, and $\rho(z) = \rho_\gamma$ for $l < z < \infty$, as is appropriate for the asymptotic limit of a macroscopically thick γ phase ($H \longrightarrow \infty$). Then from (33),

$$\sigma(l) = fl - \tfrac{1}{4}j(0)[(\rho_\alpha - \rho_\beta)^2 + (\rho_\gamma - \rho_\beta)^2] + (\rho_\beta - \rho_\alpha)(\rho_\beta - \rho_\gamma)j(l) \tag{34}$$

where

$$j(l) = 2\pi\int_{l}^{\infty}\int_{y}^{\infty}\int_{\max(b,|x|)}^{\infty} r\varphi(r)\mathrm{d}r\mathrm{d}x\mathrm{d}y \tag{35}$$

If $\varphi(r) \sim -\varphi_0/r^n$ as $r \longrightarrow \infty$, with $\varphi_0 > 0$ and $n > 4$, then

$$j(l) \sim -2\pi\varphi_0/(n-2)(n-3)(n-4)l^{n-4} \tag{36}$$

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[62] O'D. Kwon, D. Beaglehole, W. W. Webb, B. Widom, J. W. Schmidt, J. W. Cahn, M. R. Moldover, and B. Stephenson, *Phys. Rev. Lett.*, 1982, **48**, 185.

as $l \longrightarrow \infty$. The $\sigma(l)$ of (34), with this $j(l)$ and $n = 6$, is as given by de Gennes.[41] (See also Tarazona *et al.*,[44] Sullivan and Telo da Gama,[59] Dzyaloshinsky *et al.*,[63a] and Kuni *et al.*[63b]). Since ρ_β is here assumed intermediate between ρ_α and ρ_γ, the coefficient of $j(l)$ in (34) is negative, hence $1/l^{n-4}$ appears in $\sigma(l)$ in the large-l limit with positive coefficient (because $\varphi_0 > 0$ and $n > 4$). Thus, when f is small $\sigma(l)$ has its minimum at a large but microscopic l,

$$l \sim [2\pi\varphi_0(\rho_\beta - \rho_\alpha)(\rho_\gamma - \rho_\beta)/(n-2)(n-3)f]^{1/(n-3)} \tag{37}$$

With $n = 6$ and $f = (d_\beta - d_\gamma)gH$ this, too, is as found by de Gennes.[41]

When three bulk phases are in equilibrium and their tensions are related by (27), one of them, as we saw, spreads at the interface between the other two (the interface of highest tension), which, with l now macroscopic, is the configuration in Figure 9. But when the tensions are related by $\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ instead of by (27), as already remarked, this is not so; instead, the three phases meet with non-zero (and non-180°) contact angles at a common line of three-phase contact.[1,64] (One of the contact angles becomes 180° in the limiting case in which one phase is a non-deformable solid.) De Gennes[60] has called attention to the potential importance of long-range forces for the structure and energetics of such a three-phase line. There are not yet any calculations comparable to those of Tarazona *et al.*,[42–44] say, to demonstrate that the properties of that line are qualitatively different for long-range forces from what they are for short-range forces (although, in principle, calculations like those of Benner *et al.*[64] would be able to do that). The point, again, is not merely to show that different φs lead to different results but that long-rangedness *per se* has unique implications; *i.e.*, that even if a short- and a long-ranged $\varphi(r)$ shared the same zeroth and second moments a and m they would still have qualitatively different consequences. That surprising result has been amply demonstrated for films and is thus plausible also for the three-phase line, but the question is still open.

7 Conclusion

Although we have along the way seen some of the successes of current theories of phase equilibrium and interfaces, the primary purpose of this Lecture has been to call attention to discrepancies between theory and experiment, to key theoretical predictions that are still untested by experiment, and to important questions that are still unsettled even by theory. These have included the problem of the coefficient σ_0 in the surface tension near the critical point (defined by equation 1); the critical-point exponent for the vanishing of the interfacial tensions at a tricritical point; the signs of the singular terms in the tension of the non-critical interface near a critical endpoint, and the critical-point exponent for the divergence of the adsorption at that interface; the way in which a growing layer of a phase β at the interface between two other phases α and γ manifests itself in the tension of the $\alpha\gamma$ interface; the form

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[63] (*a*) I. E. Dzyaloshinsky, E. M. Lifshitz, and L. P. Pitaevsky, *Adv. Phy.*, 1961, **10**, 165; (*b*) F. M. Kuni, A. I. Rusanov, and E. N. Brodskaya, *Colloid. J. USSR* (*Engl. Transl.*), 1969, **31**, 691.

[64] R. E. Benner, Jr., L. E. Scriven, and H. T. Davis, *Faraday Symp. Chem. Soc.*, 1981, **16**, 169.

of the singularity in the surface tension of liquid helium at its lambda point; and the effect of long-ranged interactions on the structure and energetics of the line of three-phase contact.

This has left untouched two further vast areas of inquiry about interfaces, each with important unsolved problems of its own. One of these is the necessary modification [65–70] of the mean-field theory to take account of long-wavelength capillary waves, and includes the problem of whether there can be a unique deconvolution of an interfacial profile into capillary-wave and 'intrinsic' structure.[71–74] The other is the problem of curved surfaces—the surfaces of drops and bubbles of finite size—on which there has been much recent progress,[4,75–79] but where there remain some paradoxes and uncertainties. Clearly our subject is still a lively one, and has enough unanswered questions to stay that way for a long time.

Acknowledgement. This work was supported by the National Science Foundation and by the Cornell University Materials Science Center. The author thanks Dr. M. M. Telo da Gama for helpful conversations.

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[65] J. D. Weeks, *J. Chem. Phys.*, 1977, **67**, 3106.
[66] R. Evans, *Adv. Phys.*, 1979, **28**, 143.
[67] F. F. Abraham, *Phys. Rep.*, 1979, **53**, 93.
[68] J. D. Weeks, D. Bedeaux, and B. J. A. Zielinska, *J. Chem. Phys.*, 1984, **80**, 3790.
[69] D. Bedeaux and J. D. Weeks, *J. Chem. Phys.*, 1985, **82**, 972.
[70] J. K. Percus, in 'Studies in Statistical Mechanics', ed. E. W. Montroll and J. L. Lebowitz, North-Holland, 1985.
[71] D. Jasnow and J. Rudnick, *Phys. Rev. Lett.*, 1978, **41**, 698.
[72] R. Evans, *Mol. Phys.*, 1981, **42**, 1169.
[73] D. B. Abraham, *Phys. Rev. B*, 1984, **29**, 525.
[74] D. A. Huse, preprint (1984).
[75] S. J. Hemingway, J. R. Henderson, and J. S. Rowlinson, *Faraday Symp. Chem. Soc.*, 1981, **16**, 33.
[76] J. S. Rowlinson, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 77.
[77] J. S. Rowlinson, *J. Phys. A*, 1984, **17**, L357.
[78] M. P. A. Fisher and M. Wortis, *Phys. Rev. B*, 1984, **29**, 6252.
[79] P. Phillips, *Mol. Phys.*, 1984, **52**, 805.