

PHYSICAL THEORY OF FLUID INTERFACES NEAR THE CRITICAL POINT

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Abstract

A continuum theory of surfaces is developed for fluids near their critical points. The free energy of the fluid interface is considered to consist of two terms: the self free energy of inhomogeneity and an energy of interaction across the interface due to van der Waals forces. This second term is computed via the principles of Lifshitz theory and gives a physical basis to Widom's modification of the Cahn-Hilliard theory of surfaces. The scaling laws as derived by Widom are recalculated, and several differences from the original laws emerge. The theory permits calculation of absolute values of surface tensions and interface widths near the critical point from experimental dielectric and free energy data. Furthermore, the fluids considered are not necessarily simple fluids where only pairwise forces are important.

I. INTRODUCTION

It is now well established experimentally that the bulk properties of two phases in contact are not discontinuous but have a transition layer in which the various parameters characterizing the phases change continuously (e.g. Huang and Webb 1969). The width l of this layer is determined once the temperature T and pressure P of the system are specified. This width becomes very large as the critical temperature T_c is approached, and its temperature dependence is generally characterized by a negative critical exponent, $-\nu$.

The original theory of interfaces that was valid near the critical point was put forward by van der Waals (1894) and was extended significantly by Cahn and Hilliard (1958). These authors assumed that the free energy density of an inhomogeneous system could be expanded in a Taylor series in terms of the density gradients which were taken to be small. Widom (1965*a*) criticized this theory and showed that it leads to a scaling law relating the critical exponent ν to that for the surface tension, μ , which is not consistent with either experiment or numerical calculations. By replacing the Cahn-Hilliard hypothesis with the assumption that the free energy associated with an inhomogeneity of volume l^3 in the fluid remains finite as the critical temperature is approached, he deduced the now generally accepted scaling laws. While this theory has been remarkably successful, the several hypotheses which form its foundations are at best only plausible and unfortunately the theory has seen little further quantitative expression or refinement.

It is well known that the free energy of a homogeneous fluid is mainly due to the intermolecular or van der Waals forces between the molecules. Surface tension

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arises when a spatial inhomogeneity in the fluid upsets the balance of these forces. Fowkes (1962, 1963, 1964) has attempted to derive a set of rules for the determination of interfacial tensions in liquid-liquid interfaces using the measured surface tension of the liquid-vapour interface. He considered the interfacial tension to be just the sum of the surface tensions of each liquid in the presence of its vapour (i.e. due to the pull of the bulk of the liquid on the surface molecules) less the sum of the dispersion forces between two liquids across the interface (i.e. due to the pull of the one liquid on the molecules of the other across the interface). In order to determine the interfacial or surface tension of fluid interfaces near the critical point of the system, a different means of calculating the van der Waals forces must be used. This is because the interface is diffuse and is spread over many intermolecular distances. Thus we turn to Lifshitz theory of van der Waals forces which enables us to calculate the free energy of interaction of two bulk phases across a given spatial inhomogeneity. Lifshitz (1956) first calculated the van der Waals interactions of two bulk media across a vacuum, the physical meaning of which is relatively simple to understand. However, this method has been extended (Dzyaloshinskii and Pitaevskii 1959) to include all types of inhomogeneous systems where the region between the two phases is filled with a third medium which may or may not be homogeneous. In this case the van der Waals interactions of the two bulk phases are again present, even when one phase is a vacuum. Thus a finite contribution to the van der Waals free energy comes from the intervening medium. We attempt in Appendix II to explain the physical significance of the interactions in this general case.

The free energy of interaction as calculated by Lifshitz theory is not quite the same as that used by Fowkes (1962, 1963, 1964). With an appropriate choice of a self free energy of the fluid system, which is a free energy calculated *as if* there were no inhomogeneity present, we should by simple addition be able to determine the total free energy of an inhomogeneous fluid.

Besides allowing a physical interpretation to be placed on all components of the free energy of inhomogeneity in fluids, Lifshitz theory uses measured dielectric data for the fluids, and thus includes all many-body effects that are not accessible by pairwise summation techniques. The full theory has been reviewed by Dzyaloshinskii, Lifshitz, and Pitaevskii (1961), and has been much extended and simplified by others (Ninham and Parsegian 1970*a*, 1970*b*, 1970*c*; Parsegian and Ninham 1970; Richmond and Ninham 1971*a*; Davies and Ninham 1972; Mitchell and Ninham 1972).

The outline of the present paper is as follows. In Section II the fundamental assumptions of Widom's theory are discussed and equations are derived for the free energy of an inhomogeneous fluid using our hypothesis. Theoretical values of interface widths and surface tensions for nitrogen, argon, and xenon liquid-gas mixtures are calculated in Section III. These values are compared with experimental results and are shown to agree to within an order of magnitude. In Section IV the scaling laws which follow from the present theory are derived and shown to be in agreement with experiment. Finally, in Section V some observations are made concerning modifications which become necessary very near to the critical point. The scaling laws can be expected to change their form and acoustic fluctuation forces may become important, leading to the possibility of flat-topped coexistence curves in some, but not all, liquid-gas or binary mixture systems.

II. GENERAL FORMULATION

Consider a liquid and its vapour in equilibrium at pressure P and temperature T in a vertical container of length $L_1 + L_2$ and constant cross section of area A . The planar liquid-vapour interface is perpendicular to the z axis and the density ρ of the system has some profile as indicated schematically in Figure 1. The system is oriented so that as $z \rightarrow -L_2$ ($L_2 \gg l$) the density approaches that of the bulk liquid ρ_1 , and as $z \rightarrow +L_1$ ($L_1 \gg l$) the density tends to that of the homogeneous vapour ρ_g . The thickness l shown would be a reasonable (albeit arbitrary) choice for the interface thickness. The division between the two phases, i.e. the position of the plane $z = 0$, can be fixed as usual by the Gibbs criteria (Landau and Lifshitz 1959)

$$(\rho_g L_1 + \rho_1 L_2)A = N, \quad (L_1 + L_2)A = V, \quad (1a, b)$$

where V and N are the total volume and total number of molecules in the system.

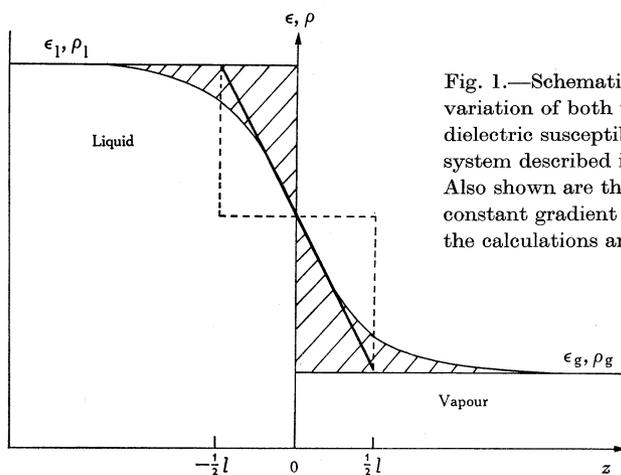


Fig. 1.—Schematic diagram of the variation of both the density ρ and dielectric susceptibility ϵ in the system described in Section II. Also shown are the single step and constant gradient interfaces used in the calculations and discussions.

It is clear that the density profile $\rho = \rho(z, l)$ must also satisfy the relation

$$A \int_{-L_2}^{L_1} \rho(z, l) dz = N. \quad (2)$$

From equations (1a) and (2) and the fact that N is a constant for the system we have

$$\int_{-L_2}^0 \{\rho(z, l) - \rho_1\} dz + \int_0^{L_1} \{\rho(z, l) - \rho_g\} dz = 0. \quad (3)$$

This equation states that the shaded areas in Figure 1 are equal. With this choice of the Gibbs dividing surface, the surface tension σ is given by (Cahn and Hilliard 1958)

$$\sigma = F(l)/A - (f_g L_1 + f_l L_2), \quad (4)$$

where $F(l)$ is the total free energy of the inhomogeneous system and f_g and f_l are the bulk free energy densities of the gas and liquid respectively.

The basic assumption of Cahn and Hilliard (1958) and Widom (1965*a*) is that $F(l)$ in equation (4) can be separated into two terms:

$$F(l) \equiv F_0(l) + F_1(l). \quad (5)$$

The first term $F_0(l)$ is a "self" energy term which is the energy of the fluid calculated as if the inhomogeneity were not present. Widom points out that this term (which is proportional to l) cannot represent the total free energy associated with the interface since the surface tension would achieve a minimum when the interface is infinitely sharp, that is, $l = 0$. The second term is essentially mathematical in character for the Cahn-Hilliard theory. This term arises from a Taylor expansion of the free energy in powers of the density gradients, and is taken to be the first (supposedly) nonzero term. Widom rewrites this term as

$$F_0(l) = \int_{-\infty}^{\infty} \kappa \{ \nabla \rho(z, l) \}^2 dz \simeq \kappa (\Delta \rho)^2 / l, \quad (6)$$

where $\Delta \rho$ is the difference in density between the two bulk phases and l is the "range" or thickness of the interface. The coefficient κ is a parameter whose temperature and density dependence is unknown, and must be fixed by experiment and guesswork (Rice 1960). The term is primarily introduced to provide a repulsive force which stabilizes the interface against the attractive self energy term. For this reason the parameter κ in equation (6) must be positive.

Thus Cahn and Hilliard's (1958) theory introduces a second term into the free energy expression (5) which has no physical basis, and is difficult to determine experimentally or theoretically. Widom's (1965*a*) extension to this theory has physical significance but is not directly amenable to quantitative calculations. We have noted that the self energy term F_0 is the free energy of the fluid calculated as if the inhomogeneity were not present, and represents an attractive force. The van der Waals interactions as calculated by Lifshitz theory only arise when an inhomogeneity is present, and are repulsive when the density changes monotonically from one phase to the other. While the self energy represents the total energy density of the fluid summed over each microscopic subvolume of the fluid, the Lifshitz interactions represent the energy required to rearrange a homogeneous fluid to give an inhomogeneous fluid. We postulate that these two contributions are distinct and together make up the total free energy. We propose therefore that

$$F(l) = F_0 + F_1 = A \int_{-L_2}^{L_1} f^\dagger \{ \rho(z, l) \} dz + AH(l, T) / l^2, \quad (7)$$

where F_0 is identified with the self energy term used by Cahn and Hilliard (1958) and Widom (1965*a*). We follow them in leaving open the question of whether in any real system the free energy density $f(\rho)$ has a complete analytical continuation $f^\dagger(\rho)$ into the unstable two-phase region (Fig. 2). The second term is the Lifshitz interaction energy written in a standard form with a generalized Hamaker constant H defined by this equation (7). This H has no physical significance of its own, but

in special cases (Appendix I) it is a constant representing the strength of the Lifshitz interactions. The Lifshitz energy may be calculated from the dispersion relation for electromagnetic surface waves in the system (van Kampen, Nijboer, and Schram 1968). In fact the l^{-2} form for this energy may be deduced from dimensional arguments.

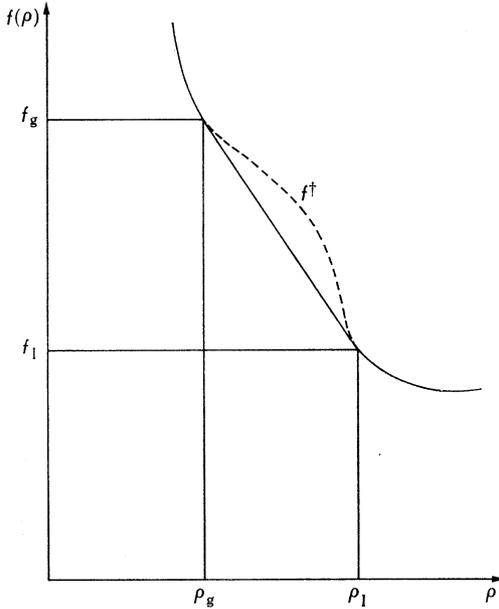


Fig. 2.—Variation of the thermodynamic free energy density $f(\rho)$ (solid curve) at a fixed temperature below the critical temperature; it is linear in the two-phase region $\rho_g < \rho < \rho_1$. The dashed curve is the continuation into the two-phase region.

In principle the density profile $\rho(z, l)$ may be calculated by minimizing the free energy with respect to variations in ρ subject to the constraint equation (3). We shall simplify the analysis by using where necessary model profiles, and simply minimize the total free energy with respect to l to determine the optimal interface thickness l_0 after the manner of Widom (1965*a*). Since H is calculated from experimental dielectric data for the fluids in the system, ϵ must be known as a function of ρ . We shall assume that this dependence is linear for simplicity (this is almost certainly true for nonpolar fluids, and may be nearly true for polar fluids near the critical point). The free energy density $f^\dagger(\rho)$ will also need to be calculated from an appropriate model as sufficient experimental or Monte Carlo data are not available to permit deduction of the analytical continuation into the two-phase region.

III. NUMERICAL CALCULATIONS WITH CRUDE MODEL INTERFACES

(a) Determination of Interface Widths

We now wish to compare the surface tensions and interface widths calculated from our theory with experimental values measured near the critical point. We assume that: (i) the shape of the interface is the same at all interfacial widths, that is,

$$\rho(z, l) = \rho(z/l) \quad \text{and} \quad \epsilon(z, l) = \epsilon(z/l),$$

and (ii) the interface is not wide enough for retardation effects to predominate. It is shown in the first section of Appendix I that H is independent of l in this case. Thus equation (7) becomes

$$F(l) = A \int_{-L_2}^{L_1} f\{\rho(z/l)\} dz + AH(T)/l^2. \quad (8)$$

Minimizing this with respect to l and allowing L_1 and L_2 to approach infinity, we have the equilibrium interface width

$$l_0 = (2H/D)^{\frac{1}{2}}, \quad (9)$$

where

$$D = \int_0^\infty \{f(\rho(u)) - f_g\} du + \int_0^\infty \{f(\rho(-u)) - f_l\} du \quad (10)$$

and $u = z/l$. Equation (4) yields the surface tension

$$\sigma = 3H/l_0^2. \quad (11)$$

Note Added in Proof

Rusanov (1971; *Recent Prog. Surface Membrane Sci.* 4, 59) has put forward a theory of fluid interfaces which is based on long range van der Waals forces. He derives an interface width l_0 identical with our equation (9) by using rigorous statistical mechanical techniques. This gives rise to the same scaling laws as the present results (see Section IV).

(b) Widom's Theory of Free Energy

The self energy term F_0 requires a knowledge of both the interface shape $\rho(z/l)$ and the free energy density f of the homogeneous fluid with its analytical continuation into the two-phase region. Widom (1965*b*) has proposed a general form for the chemical potential of fluids near the critical point, which is suitable for use here. A difficulty with this chemical potential is that it is in terms of an unknown function of density and temperature, which has only a few restrictions on its form. Griffiths (1967) has examined the suitability of several different functions and Fisk and Widom (1969) have given a further set of functions which can be used in a practical calculation. Unfortunately they are all arbitrary to some degree.

Widom's (1965*b*) postulate reduces to

$$\mu(\rho, T) - \mu(\rho_c, T) = (\rho - \rho_c) \{T - \tau(\rho)\} (T_c - T)^{\gamma-1} j \{ \{T_c - \tau(\rho)\} / (T_c - T) \}, \quad (12)$$

where $\tau(\rho) = T_c - a(\rho - \rho_c)^{1/\beta}$ is the equation for the temperature along the coexistence curve and j is an arbitrary function of $\{T_c - \tau(\rho)\} / (T_c - T)$. Here ρ is the density, T is the temperature, μ is the chemical potential, γ and β are critical exponents, and a is a constant, while the subscripts c refer to values at the critical point. The Helmholtz free energy density $f(\rho)$ is given by $\mu = (\partial f / \partial \rho)_T$, so that equation (12) gives

$$f(\rho) - f(\rho_c) = \frac{(1 - T/T_c)^{2\beta + \gamma} j(1)}{\gamma a^{2\beta}} \int_0^y y' q(y') dy' + \frac{(\Delta T)^\beta}{\alpha^\beta} \mu(\rho_c, T) y, \quad (13)$$

where

$$q(y) = \gamma(y^{1/\beta} - 1)j(y^{1/\beta})/j(1), \quad y = a^\beta(\rho - \rho_c)/(T_c - T)^\beta, \quad (14, 15)$$

and $j(1)$ is a constant.

From equations (10) and (13) and the condition (3) we get

$$D = \int_0^\infty \{f(\rho(u)) - f_g\} du + \int_0^\infty \{f(\rho(-u)) - f_l\} du = \{(1 - T/T_c)^{2\beta+\gamma} j(1)/\gamma a^{2\beta}\} B, \quad (16)$$

where

$$B = \int_0^\infty \left(\int_{y(u)}^1 x q(x) dx - \int_{-1}^{y(-u)} x q(x) dx \right) du \quad (17)$$

is a constant depending only on the functional form $q(x)$ for the chemical potential and the equation $y(u)$ of the interface profile. Here u is the scaled distance z/l as used in equation (10). Fisk and Widom (1969) used the function

$$q(x) = 1 - x^4,$$

which satisfies experiment and most of the mathematical thermodynamic conditions for the chemical potential. The interfacial profile $y(u)$ which they derived has been shown by Huang and Webb (1969) to fit experiment reasonably well, and so we shall use their value $B = 0.31$ directly in equation (16). With the relationships

$$\rho_1^2 \chi(\rho_1) = (1 - T/T_c)^{-\gamma} / j(1)$$

for the compressibility and

$$a^{2\beta} = 4(1 - T/T_c)^{2\beta} / (\rho_1 - \rho_g)^2,$$

derived from Widom's (1965*b*) equation of state (12), we may write (16) as

$$D = \{(\rho_1 - \rho_g)^2 / 4\gamma \rho_1^2 \chi(\rho_1)\} B. \quad (18)$$

This is now suitable for use with experimental density and compressibility data.

(c) Calculation of Lifshitz Free Energy

The Hamaker constant H was calculated using a different model interface for which the mathematics and numerical computations are not too complicated (see Appendix I). This model was the constant gradient interface as shown in Figure 1. It approximates the interface by a linear interpolation between liquid and gas densities over the distance l . The present use of two different models to calculate the self energy and van der Waals energy contributions is not inconsistent as the two calculations are completely independent.

Numerical values of the Hamaker constant derived in Appendix I were calculated by computer using the dielectric susceptibilities for liquid

$$\epsilon_1(i\xi_n) = \epsilon_D = 1 + (n_R^2 - 1)/(1 + \xi_n^2/\omega^2), \quad \xi_n < \omega, \quad (19a)$$

$$= \epsilon_p = 1 + 4\pi N e^2 / m \xi_n^2, \quad \xi_n > \omega', \quad (19b)$$

$$= [\{\epsilon_p(\omega') - \epsilon_D(\omega)\}/(\omega' - \omega)](\xi_n - \omega) + \epsilon_D(\omega), \quad \omega < \xi_n < \omega', \quad (19c)$$

and for gas

$$\epsilon_g = 1.$$

The expression (19a) is an adapted Lorentz representation appropriate to a nonpolar fluid with only a single ultraviolet absorption at frequency ω ; here n_R is the refractive index and $\omega = eI/\hbar$ is the absorption frequency, I being the ionization potential of the fluid molecules and e the electronic charge. The second representation (19b) is the plasma dielectric susceptibility due to the electronic cloud around the molecules; here N is the number density of the electrons and m is the electronic mass. In the region between ω and ω' the electronic spectrum is usually very complicated, and we have chosen a linear interpolation after the suggestion of Ninham and Parsegian (1970a). This choice is arbitrary to some degree and will introduce an uncertainty in the non-retarded calculations of van der Waals forces. This is of no importance in an order of magnitude calculation.

We have taken values of refractive index in (19) which are appropriate to temperatures far from the critical point. This is to avoid the influence of critical fluctuations in dielectric susceptibilities which make calculations of the Hamaker constant difficult. The effect of fluctuations on scaling laws is estimated qualitatively in Section IV. For numerical calculations, however, we need to concentrate on regions where these fluctuations are small but where the approximation (i) in Section III(a) for the density profile is still reasonable. These calculations may then be extrapolated using scaling laws derived in Section IV. The fully quantitative calculations including fluctuations must await further developments in Lifshitz theory.

(d) Data Used in Calculations

The results of the theoretical calculations of H and D are listed in Table 3 for the liquids nitrogen, argon, and xenon. Values of H for the polar liquid mixtures cyclohexane-methanol and cyclohexane-aniline were calculated from modified forms of equations (19) to account for the large microwave contributions to the dielectric susceptibility.

Experimental data used in the calculation of H and D are given in Table 1. In this table each entry for the density and compressibility is the factor ζ_0 and the accompanying value in parentheses is the experimental critical exponent θ in the scaled equation

$$\zeta = \zeta_0(1-T/T_c)^\theta,$$

where ζ is the quantity appropriate to each column. (This scheme is repeated for the experimental values in Tables 2 and 3.) For the calculations of H , dielectric data were taken from Hodgman *et al.* (1971). The refractive index of liquid xenon was taken from Garside, Molgaard, and Smith (1968). For the calculations of D , compressibility data for xenon were from Smith and Benedek (to be published) and for nitrogen and argon from Fisk and Widom (1969) and Buff and Lovett (1968) respectively, while density and surface tension data were from Smith, Gardner, and Parker (1967) but for xenon from Zollweg, Hawkins, and Benedek (1971). The data for the correlation length ξ for nitrogen and argon were taken from Fisk and Widom (1969).

They calculated ξ values from compressibility data, which in turn were calculated by numerical differentiation of PVT data (Thomas and Schmidt 1963, 1964). The latter are not very reliable estimates. The correlation length data for xenon were taken from Giglio and Benedek (1969). By far the most accurate compressibility data in Table 1 are for xenon. The calculated values of interface width l_0 and surface tension σ as functions of temperature are given in Table 2.

TABLE 1
DATA USED IN CALCULATIONS

The values in parentheses are the measured critical exponents (see Section III(d))

Fluid	$\rho_l - \rho_g$ (g cm ⁻³)	$\rho^2 \chi(\rho)$ (g ² erg ⁻¹ cm ⁻³)	n_R	I (eV)
Nitrogen	1.11 (0.317)	6.39×10^{-10} (-1.23)	1.2053	14.53
Argon	1.88 (0.341)	5.48×10^{-11} (-1.24)	1.23	15.755
Xenon	3.98 (0.345)	3.46×10^{-10} (-1.21)	1.2	12.127

TABLE 2

COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF INTERFACE WIDTH l_0 AND SURFACE TENSION σ

The experimental interface widths are taken to be $l_0 = \sqrt{24} \xi$, where ξ is the correlation length, as discussed in the text. The values in parentheses are the measured critical exponents

Fluid	$l_0(\text{exp.})$ (Å)	$l_0(\text{theory})$ (Å)	$\sigma(\text{exp.})$ (erg cm ⁻²)	$\sigma(\text{theory})$ (erg cm ⁻²)
Nitrogen	5.14 (-0.624)	6.59	29.1 (1.241)	37.6
Argon	3.09 (-0.64)	5.18	38.1 (1.281)	106.4
Xenon	6.81 (-0.598)	5.89	62.9 (1.302)	89.7

(e) Experimental Interface Widths

In order to compare the theoretical values of l_0 with correlation length data, it is necessary to relate the two. Huang and Webb (1969) considered this problem and proposed several different definitions of interface width in order to find a suitable measure. The "exponential" definition is: as $z \rightarrow \infty$ say, the interfacial profile $\rho(z/l)$ will have the asymptotic form

$$\rho_l - \rho(z/l) \sim K \exp(-z/l'),$$

where K is a constant. The interface width l' defined through this relation is identical with the correlation length ξ (Fisk and Widom 1969). The second definition we consider is the "central gradient" definition: the interface width l_0 is defined as the width of a constant gradient interface having the same slope as that of the real interface at the origin $z = 0$. This latter definition is identical with that of our model

interface used to calculate the Hamaker constant. Now the relation between these two definitions of interface width l_0 and l' depends on the actual interfacial profile. For the tanh profile, derived from Cahn and Hilliard's (1958) theory of interfaces applied to a classical van der Waals liquid, we have

$$l' = \xi = l_0/4.$$

But for the Fisk and Widom (1969) profile, which we used for our calculations of D ,

$$l' = \xi = l_0/\sqrt{24}. \quad (20)$$

For other profiles, Huang and Webb (1969) have given a list of connecting factors between ξ and l_0 . Because the Fisk and Widom profile appears to fit the Huang and Webb experimental data closely, we assume this to be the actual profile and use the relation (20). This is of course another source of error in our comparison of theory and experiment. Again we emphasize that these errors will be unimportant in an order of magnitude calculation.

TABLE 3

COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF HAMAKER CONSTANT H AND SELF ENERGY FACTOR D

Two binary mixtures for which free energy data are not available are also compared. The values in parentheses are the measured critical exponents

Fluid	$H(\text{exp.})$ (10^{-16} erg)	$H(\text{theory})$ (10^{-16} erg)	$D(\text{exp.})$ (10^8 erg cm $^{-3}$)	$D(\text{theory})$ (10^8 erg cm $^{-3}$)
Nitrogen	254 (−0.001)	544	3.771 (1.865)	3.49
Argon	120 (0.001)	952	8.229 (1.92)	11.27
Xenon	973 (0.106)	1040	6.158 (1.9)	10.14
Cyclohexane-methanol	578–3024 (−0.11)	440	—	—
Cyclohexane-aniline	1838 (0.16)	488	—	—

(f) *Comparison of Theory with Experiment*

In Table 2, the experimental interface widths $l_0 = \sqrt{24} \xi$ and surface tensions are compared with theoretical values from equations (9) and (11), while in Table 3 theoretical values of the Hamaker constant H and self energy term D are compared with the experimental values

$$H = \frac{1}{3}\sigma l_0^2 = 8\sigma\xi^2, \quad D = \frac{2}{3}\sigma/l_0 = \sigma/\sqrt{54}\xi.$$

This latter separation allows the comparison of each of the two independent calculations in our theory. The experimental value of H for argon is low by a factor of eight, but in general the order of magnitude comparison is very good. This indicates that dispersion forces, if not the only contributing force, at least give a substantial contribution to the stability of the interface in fluid systems.

IV. SCALING LAW ANALYSIS

We now consider the consequences of our theory. The critical exponents μ , ν , and ν are defined by

$$\sigma \propto |T_c - T|^\mu, \quad l_0 \propto |T_c - T|^{-\nu}, \quad H \propto |T_c - T|^\nu,$$

which immediately give the scaling laws from equation (9)

$$3\nu = 2\beta + \gamma - \nu \quad (21)$$

and from equation (11)

$$\mu = 2\nu + \nu. \quad (22)$$

Eliminating ν from these equations gives

$$\mu + \nu = 2\beta + \gamma,$$

which is one of the scaling laws postulated by Widom (1965*a*) to be common to all theories of surfaces. To find the exponent ν we must look very closely at the expressions for the Hamaker constant H . It is possible to show analytically that to a good approximation

$$H \propto (\epsilon_1 - \epsilon_g)^2 \quad (23)$$

for our model interface. We expect this to be true for any type of interface near the critical point. In polar fluids the actual temperature dependence of $\epsilon_1 - \epsilon_g$ is uncertain, although some experimental work suggests that it may be divergent with a similar power law type of singularity to that of the specific heat (Arkhangelski and Semchenko 1967; Snider 1971). In nonpolar liquids Garside, Molgaard, and Smith (1968) have demonstrated that to very good accuracy

$$(\epsilon_1 - \epsilon_g) \propto (\rho_l - \rho_g) \propto |T_c - T|^\beta, \quad (24)$$

where the critical exponent $\beta \approx \frac{1}{3}$. This means that ν as given via equation (23) is of the order of 0.7, which is well in excess of the value of ν deduced from any experiment.

It is possible that the discrepancy lies in the neglect of fluctuations in the system. The self energy includes implicitly all those fluctuations which would occur in a homogeneous system. We need some estimate of the difference between the root mean square amplitude of fluctuations in the actual system and those in the virtual homogeneous system. We now postulate that the temperature dependence of H is not that defined in equation (23) but is in fact

$$H \propto (\langle \nu^2 \rangle^{\frac{1}{2}} - \langle \nu^2 \rangle_h^{\frac{1}{2}})^2 = (\delta\rho)_{\text{fluct}}^2, \quad (25)$$

where the subscript h refers to the homogeneous system and ν is the fluctuation amplitude $\rho - \langle \rho \rangle$ at some representative point in the interface, most likely where the fluctuation amplitude is a maximum. The Ornstein-Zernike fluctuation theorem

(Landau and Lifshitz 1959, Section 115) states that

$$V \langle v_1(\mathbf{r}_1)^2 \rangle_h = \int_V \langle v_1(\mathbf{r}_1) v_1(\mathbf{r}_2) \rangle d\mathbf{r}_2 = kT \rho^2 \chi(\rho), \quad (26)$$

where $\rho = \rho(\mathbf{r}_1)$ and V is some small volume in the fluid. The subscript 1 refers to fluctuations in a fluid of average density $\langle \rho(\mathbf{r}_1) \rangle$. The first relationship states that the mean square fluctuation amplitude at any point in the homogeneous fluid is the sum of all correlations over the volume V . If we extend this idea to inhomogeneous systems, we may generalize equation (26) to

$$\langle v_1(\mathbf{r}_1)^2 \rangle = \int_V \langle v_1(\mathbf{r}_1) v_2(\mathbf{r}_2) \rangle V^{-1} d\mathbf{r}_2, \quad (27)$$

where v_2 is the fluctuation in a fluid of mean density $\langle \rho(\mathbf{r}_2) \rangle$. Now define

$$\delta v(\mathbf{r}_2) = v_2(\mathbf{r}_2) - v_1(\mathbf{r}_1),$$

so that using (27)

$$\langle v_1(\mathbf{r}_1)^2 \rangle = \langle v_1(\mathbf{r}_1)^2 \rangle_h + \int_V \langle v_1(\mathbf{r}_1) \delta v(\mathbf{r}_2) \rangle V^{-1} d\mathbf{r}_2. \quad (28)$$

Taking the square root of both sides of (28) gives

$$\langle v_1(\mathbf{r}_1)^2 \rangle^{\frac{1}{2}} = \langle v_1(\mathbf{r}_1)^2 \rangle_h^{\frac{1}{2}} \left(1 + \frac{1}{\langle v_1(\mathbf{r}_1)^2 \rangle_h} \int_V \langle v_1(\mathbf{r}_1) \delta v(\mathbf{r}_2) \rangle V^{-1} d\mathbf{r}_2 \right)^{\frac{1}{2}}.$$

If we now expand the square root, substitute into equation (25), and neglect higher order terms, we have

$$H \propto \frac{1}{\langle v_1(\mathbf{r}_1)^2 \rangle_h} \left(\int_V \langle v_1(\mathbf{r}_1) \delta v(\mathbf{r}_2) \rangle V^{-1} d\mathbf{r}_2 \right)^2. \quad (29)$$

Expanding about z_1 ,

$$\langle v_1(\mathbf{r}_1) \delta v(\mathbf{r}_2) \rangle = (z_2 - z_1) \frac{d}{dz_2} \left(\langle v_1(\mathbf{r}_1) v_2(\mathbf{r}_2) \rangle_{z_2=z_1} \right) + \dots = \frac{z_2 - z_1}{2} \frac{d \langle v_1(\mathbf{r}_1)^2 \rangle}{dz_1} + \dots,$$

and equation (29) becomes

$$H \propto \frac{1}{\langle v_1(\mathbf{r}_1)^2 \rangle_h} \left(V^{-1} \int_V (z_2 - z_1) d\mathbf{r}_2 \frac{d \langle v_1(\mathbf{r}_1)^2 \rangle}{dz_1} \right)^2 + \dots \quad (30)$$

The volume V is just the volume of the interface $V = Al$ and, since

$$\int_V z_2 d\mathbf{r}_2 = 0$$

by symmetry, we have

$$H \propto \frac{1}{\langle v_1(\mathbf{r}_1)^2 \rangle_h} \left(z_1 \frac{d \langle v_1(\mathbf{r}_1)^2 \rangle}{dz_1} \right)^2.$$

All higher order terms in the expansions here have been neglected since they are smaller than the first term near the critical point. Now

$$\langle v_1(\mathbf{r}_1)^2 \rangle \approx \langle v_1(\mathbf{r}_1)^2 \rangle_h$$

to first order, so that from equation (26)

$$\begin{aligned} (\delta\rho)_{\text{fluct}}^2 &\propto \left\{ z_1 \frac{d}{dz_1} \left(\frac{kT\rho^2\chi(\rho)}{V} \right) \right\}^2 / \frac{kT\rho^2\chi(\rho)}{V} \\ &\propto (2kT/V)\chi(\rho) (z_1 d\rho/dz_1)^2 + T_2, \end{aligned}$$

where T_2 is a term in $\chi'(\rho)$. Here the first term is a maximum for $z_1 \sim l$, and the second term is of the same order as the first term, so that we have finally

$$H \propto (2kT/Al)\chi(\rho) (l d\rho/dz)^2 \propto \Delta T^{2\beta-\gamma+\nu}$$

or

$$\nu = 2\beta - \gamma + \nu. \quad (31)$$

Putting the scaling law (31) into equation (21) gives

$$\nu = \frac{1}{2}\gamma, \quad (32)$$

which is that derived by Widom (1965*a*) on the assumptions of Cahn and Hilliard's (1958) theory. This scaling law does not hold in such rigorous model systems as the Ising model. We note, however, that a very recent experiment of Zollweg, Hawkins, and Benedek (1971) showed that for xenon the critical exponents were

$$\mu = 1.302 \pm 0.006, \quad \nu = 0.57 \pm 0.05, \quad \gamma = 1.21 \pm 0.03, \quad \beta = 0.345 \pm 0.01,$$

which gave

$$\mu + \nu - (\gamma + 2\beta) = -0.03 \pm 0.06, \quad \mu - 2\nu = 0.16 \pm 0.1, \quad \gamma - 2\nu = 0.07 \pm 0.13.$$

For this experiment the scaling law

$$\mu = 2\nu$$

does not hold within experimental error, but the scaling law of Cahn and Hilliard (equation (32)) holds well. It seems possible that, for various different real fluids, scaling laws and critical exponents will also be different. We also note that another recent experiment with carbon dioxide (Lunacek and Canell 1971) yields values of ν and γ which do not satisfy equation (32) to within experimental error. A value for μ has not yet been accurately measured in this case.

The purpose of this section has been to demonstrate that scaling laws derived from our theory are not completely inconsistent with experiment. The Taylor expansions used to derive these scaling laws may not be valid, as was pointed out by Widom (1965*a*) concerning the Taylor expansions in the Cahn-Hilliard (1958) theory. More work needs to be done in this area.

V. DISCUSSION

Besides the scaling laws discussed in the previous section, several other speculations may be made about the consequences of our theory.

(a) Retardation Effects

As the critical point is approached and the interface width l increases, retardation effects in the van der Waals interaction will become important. We expect this to occur when $l \approx 100 \text{ \AA}$. Determination of the temperature dependence of the Hamaker function $H(l, T)$ is difficult, as we have noted, but we can state qualitatively

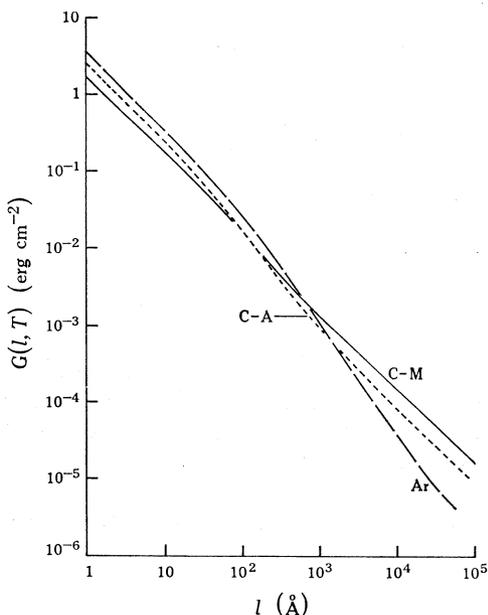


Fig. 3.—Functional dependence of van der Waals or Lifshitz energies with the interface width l on a log-log plot. The interaction energies are calculated from a single step interfacial profile model for mixtures of cyclohexane (C) with the two polar fluids methanol (M, $\epsilon_0 = 32$) and aniline (A, $\epsilon_0 = 6$) and for the nonpolar fluid argon ($\epsilon_0 = 1.513$). The differences in retarded behaviour are clearly shown by these curves.

how the force changes as the critical point is reached. For simple fluids such as argon and xenon which have a step interface profile as in Figure 1, retardation effects lead to an interaction energy proportional to l^{-3} . This behaviour is shown for argon in Figure 3. For more complex polar fluids, retardation effects will not cause the van der Waals force to decrease as rapidly with l as for nonpolar fluids, since a new component of the energy, due to Debye relaxation of permanent dipole moments, will become important. This contribution is proportional to l^{-2} but the proportionality constant is somewhat reduced from the Hamaker constant. The resultant behaviour of the van der Waals interaction energy is illustrated again in Figure 3 for the two polar fluid mixtures cyclohexane-methanol and cyclohexane-aniline. The latter system has been studied by Atack and Rice (1953, 1954). Because aniline is less polar than methanol, the kink in the curve around $l \sim 100 \text{ \AA}$ is larger.

Thus for the nonpolar fluid systems where the van der Waals energy becomes proportional to l^{-3} , the scaling laws deduced above will break down. It is not possible to perform full calculations of van der Waals forces in continuously inhomogeneous

systems. However, if they are approximated by "cell" type interfaces made up of many small regions of constant average density, full retarded calculations may be performed. The work of Ninham and Parsegian (1970*a*, 1970*c*) illustrates that in fact the same qualitative conclusions will carry over to this more general case.

(b) *Flat-topped Coexistence Curve*

The self energy F_0 and the van der Waals interaction energy F_1 need not be the only energies which contribute to the stability of the interface. Dzyaloshinskii, Lifshitz, and Pitaevskii (1961) at the end of their review suggest that an interaction energy may arise from acoustic fluctuations. Although this certainly contributes to the forces acting in the fluid close to the critical point, no quantitative predictions of its magnitude are possible. However, these authors do show that for a step interface the force takes the form

$$F_A = AH_A/l^2,$$

with the "acoustic" Hamaker constant

$$H_A \propto (n_l^2 - n_i^2)(n_g^2 - n_i^2),$$

where n is the zero-frequency acoustic refractive index and the suffixes l, i, and g refer to liquid, interface, and gas respectively. The major difficulty here is to understand how n_i varies across the interface of a liquid-gas or binary liquid mixture system. If it varies monotonically as do the density and dielectric susceptibilities, then the energy F_A will be repulsive and simply add to the electromagnetic Lifshitz energy. We had previously assumed (Sarkies, Ninham, and Richmond 1971) that the acoustic refractive index in the interface would rapidly attain a value much smaller than that of both the liquid and gas phases. This argument was based on estimates of compressibilities from the Cahn-Hilliard (1958) theory. If this is true, then F_A is an attractive force which will eventually swamp the retarded electromagnetic forces at some temperature $T_1 < T_c$. Then the surface tension will become zero and the interface will collapse. At any temperature between T_1 and T_c , the fluid phases will mix homogeneously because of density fluctuations in the system and a flat top will be observed on the coexistence curve. The meniscus will not be visible in this region, giving the impression that T_1 is the critical temperature. The phenomenon has been observed by Atask and Rice (1953, 1954).

(c) *Restrictions on Retarded Behaviour*

Bullough (1970) discusses in his series of papers on many-body optics the variation of the dielectric susceptibility with distance in bulk fluids. He relates this to the pair distribution function $g(r)$. At the end of his paper he shows that his "complex" dielectric susceptibility in the continuum approximation reduces to the physical dielectric susceptibility which we used in our work, provided $\omega \ll c/l$, where ω is the frequency of electromagnetic radiation propagating through the fluid and l is a correlation length.

In all simple nonpolar fluids, ω for the dominating electromagnetic interactions is less than about 10^{16} rads^{-1} , and the condition on l is that it be less than about

100 Å. This means that our treatment of the retarded interactions above may need to be modified. At present we are conducting further research into the problem. For polar fluids at larger values of l , the dominating electromagnetic interactions occur at much lower frequencies. We expect in fact that no restriction will need to be placed on the values of l in this case.

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VII. REFERENCES

- ARKHANGELSKI, K. V., and SEMENCHENKO, V. K. (1967).—*Russ. J. phys. Chem.* **41**, 4296.
- ATAK, D., and RICE, O. K. (1953).—*Discuss. Faraday Soc.* **15**, 210.
- ATAK, D., and RICE, O. K. (1954).—*J. chem. Phys.* **22**, 382.
- BUFF, F. P., and LOVETT, R. A. (1968).—In "Simple Dense Fluids; Data and Theory". (Eds. Z. W. Salzburg and H. L. Frisch.) (Academic Press: New York.)
- BULLOUGH, R. K. (1970).—*J. Phys. A* **3**, 708.
- CAHN, J. W., and HILLIARD, J. E. (1958).—*J. chem. Phys.* **28**, 258.
- DAVIES, B., and NINHAM, B. W. (1972).—*J. chem. Phys.* **56**, 5797.
- DZYALOSHINSKII, I. E., LIFSHITZ, E. M., and PITAEVSKII, L. P. (1961).—*Adv. Phys.* **10**, 165.
- DZYALOSHINSKII, I. E., and PITAEVSKII, L. P. (1959).—*Soviet Phys. JETP* **9**, 1282.
- FISK, S., and WIDOM, B. (1969).—*J. chem. Phys.* **50**, 3219.
- FOWKES, F. M. (1962).—*J. phys. Chem.* **66**, 382.
- FOWKES, F. M. (1963).—*J. phys. Chem.* **67**, 2538.
- FOWKES, F. M. (1964).—*J. ind. Engng Chem.* **56**(12), 40.
- GARSDALE, D. H., MOLGAARD, H. V., and SMITH, B. L. (1968).—*J. Phys. B* **1**, 449.
- GIGLIO, M., and BENEDEK, G. B. (1969).—*Phys. Rev. Lett.* **23**, 1145.
- GRIFFITHS, R. B. (1967).—*Phys. Rev.* **158**, 176.
- HODGMAN, C. D., et al. (Eds.) (1971).—"Handbook of Physics and Chemistry." 35th Ed. pp. 1872–2661. (Chemical Rubber Publishing Co.: Cleveland, Ohio.)
- HUANG, J., and WEBB, W. W. (1969).—*J. chem. Phys.* **50**, 3677.
- VAN KAMPEN, N. G., NIJBOER, B. R. A., and SCHRAM, K. (1968).—*Phys. Lett. A* **26**, 307.
- LANDAU, L. D., and LIFSHITZ, E. M. (1959).—"Statistical Physics." (Pergamon Press: London.)
- LIFSHITZ, E. M. (1956).—*J. exp. theor. Phys.* **2**, 73.
- LUNACEK, J. H., and CANELL, O. S. (1971).—*Phys. Rev. Lett.* **27**, 841.
- MITCHELL, D. J., and NINHAM, B. W. (1972).—*J. chem. Phys.* **56**, 1117.
- NINHAM, B. W., and PARSEGAN, V. A. (1970a).—*J. chem. Phys.* **52**, 4578.
- NINHAM, B. W., and PARSEGAN, V. A. (1970b).—*Biophys. J.* **10**, 646.
- NINHAM, B. W., and PARSEGAN, V. A. (1970c).—*J. chem. Phys.* **53**, 3398.
- NINHAM, B. W., PARSEGAN, V. A., and WEISS, G. H. (1971).—*J. stat. Phys.* **2**, 323.
- PARSEGAN, V. A., and NINHAM, B. W. (1970).—*Biophys. J.* **10**, 664.
- RICE, O. K. (1960).—*J. phys. Chem.* **64**, 976.
- RICHMOND, P., and NINHAM, B. W. (1971a).—*J. Low Temp. Phys.* **5**, 177.
- RICHMOND, P., and NINHAM, B. W. (1971b).—*J. Phys. C* **4**, 1988.
- SARKIES, K. W., NINHAM, B. W., and RICHMOND, P. (1971).—*J. Phys. C* **4**, L235.
- SMITH, B. L., GARDNER, P. R., and PARKER, E. H. C. (1967).—*J. chem. Phys.* **47**, 1148.
- SNIDER, N. S. (1971).—*J. chem. Phys.* **55**, 3994.
- THOMAS, J. E., and SCHMIDT, P. W. (1963).—*J. chem. Phys.* **39**, 2506.
- THOMAS, J. E., and SCHMIDT, P. W. (1964).—*J. Am. chem. Soc.* **86**, 3554.
- VAN DER WAALS, J. D. (1894).—*Z. phys. Chem.* **13**, 657.
- WIDOM, B. (1965a).—*J. chem. Phys.* **43**, 3892.
- WIDOM, B. (1965b).—*J. chem. Phys.* **43**, 3898.
- ZOLLWEG, J., HAWKINS, G., and BENEDEK, G. B. (1971).—*Phys. Rev. Lett.* **27**, 1182.

APPENDIX I

(a) *Non-retarded van der Waals Forces*

We show here that, for non-retarded van der Waals forces when the effect of the finite velocity of light is negligible,

$$F_1 = AH/l^2,$$

where H is independent of l regardless of the shape of the interface. The only condition is

$$\rho(z, l) = \rho(z/l). \quad (\text{A1})$$

Lifshitz theory calculates the interaction of surface electromagnetic modes which are set up in the system by random temperature fluctuations and zero point fluctuations in the material of the bulk phases. The electric potential ϕ for these surface modes in a medium of non-uniform dielectric constant $\epsilon\{\rho(z, l)\}$ is given by

$$\nabla \cdot (\epsilon \nabla \phi) = 0. \quad (\text{A2})$$

As ϵ changes only in the z direction, we may write

$$\phi = u(z) \exp\{i(wx + vy)\}, \quad (\text{A3})$$

where w and v are the propagation numbers for the x and y directions respectively. From equations (A2) and (A3) we can deduce

$$\frac{d^2 u}{dz^2} + \frac{d\{\ln \epsilon(\rho)\}}{dz} \frac{du}{dz} - k^2 u = 0. \quad (\text{A4})$$

Invoking the condition (A1) we introduce a new variable $x = z/l$ and equation (A4) then becomes

$$\frac{d^2 u}{dx^2} + \frac{d\{\ln \epsilon(\rho(x))\}}{dx} \frac{du}{dx} - (kl)^2 u = 0.$$

Because this equation has only one parameter kl , the resulting dispersion relation for the modes of the system will be

$$D(k; \omega; l) = D(kl; \omega) = 0.$$

The free energy per unit area for van der Waals interactions can now be written down immediately in terms of this dispersion relation (van Kampen, Nijboer, and Schram 1968; Ninham, Parsegian, and Weiss 1971; Richmond and Ninham 1971b):

$$G(l, T) = (k_B T / 2\pi) \sum'_{n=0} \int_0^\infty dk k \ln D(kl; i\xi_n), \quad (\text{A5})$$

where $\xi_n = 2\pi k_B T n / \hbar$. By change of variable from k to kl in the integral, equation (A5) can be written

$$G(l, T) = H(T) / l^2,$$

where

$$H(T) = (k_B T/2\pi) \sum_{n=0}^{\infty} \int_0^{\infty} dy y \ln D(y; i\xi_n)$$

which is independent of l .

(b) *Dispersion Relation for Constant Gradient Interface*

For a constant gradient interface (Fig. 1) the dielectric susceptibilities may be written

$$\begin{aligned} \epsilon(z/l) &= \epsilon_1, & z < -\frac{1}{2}l, \\ &= \frac{1}{2}(\epsilon_1 + \epsilon_2) - (\epsilon_1 - \epsilon_2)z/l, & -\frac{1}{2}l < z < \frac{1}{2}l, \\ &= \epsilon_2, & z > \frac{1}{2}l. \end{aligned}$$

Substituting into equation (A4) we get

$$\begin{aligned} u_1 &= A \exp(kz), & z < -\frac{1}{2}l, \\ u_1 &= BI_0(\frac{1}{2}k(z-l\delta)) + CK_0(\frac{1}{2}k(z-l\delta)), & -\frac{1}{2}l < z < \frac{1}{2}l, \\ u_2 &= E \exp(-kz), & z > \frac{1}{2}l, \end{aligned}$$

where I_0 and K_0 are the zero-order modified Bessel functions and

$$\delta = (\epsilon_1 + \epsilon_2)/(\epsilon_1 - \epsilon_2).$$

Here only the surface modes ($u \rightarrow 0$ as $z \rightarrow \pm \infty$) have been considered.

Using the boundary conditions that $u(z)$ and du/dz are continuous across each boundary at $z = \pm \frac{1}{2}l$, we get the dispersion relation

$$\begin{aligned} 0 = D(kl; \omega) &= 1 - \frac{K_0(kl\delta_1) - K_1(kl\delta_1) I_0(kl\delta_2) - I_1(kl\delta_2)}{K_0(kl\delta_1) + K_1(kl\delta_1) I_0(kl\delta_2) + I_1(kl\delta_2)}, & \epsilon_1 > \epsilon_2, \\ &= 1 - \frac{K_0(kl\delta_2) - K_1(kl\delta_2) I_0(kl\delta_1) - I_1(kl\delta_1)}{K_0(kl\delta_2) + K_1(kl\delta_2) I_0(kl\delta_1) + I_1(kl\delta_1)}, & \epsilon_1 < \epsilon_2, \end{aligned}$$

where $\delta_1 = |\epsilon_1/(\epsilon_1 - \epsilon_2)|$ and $\delta_2 = |\epsilon_2/(\epsilon_1 - \epsilon_2)|$. The $D(kl; \omega)$ defined in this way approaches unity as $k \rightarrow \infty$, as required for the convergence of the integral (A5). It is not discontinuous across the line $\epsilon_1 = \epsilon_2$ but is in fact analytically continued across this line.

APPENDIX II

Physical Significance of Lifshitz Interactions

We have noted in the Introduction that the calculation of van der Waals forces between two bulk phases via Lifshitz theory gives rise to a finite energy even when one or both of the phases is a vacuum. The intervening medium must be different from both bulk phases in the value of its dielectric constant at any point, or it may be inhomogeneous, in order for this energy to be nonzero. However, if the

intervening medium is identical with one or both of the bulk phases, and is homogeneous, no interaction will occur. Thus the Lifshitz interactions arise from the presence of any spatial inhomogeneity in the system. Applied to our fluid interface (Fig. 4) we see that the inhomogeneity has a spatial extent, and will thus have a finite energy of interaction even though the gaseous phase is almost a vacuum. As the van der Waals forces are most easily understood when acting in homogeneous systems (except for sharp boundaries which have no spatial extent by themselves), we shall divide the interface into n approximately homogeneous cells as illustrated in Figure 4.

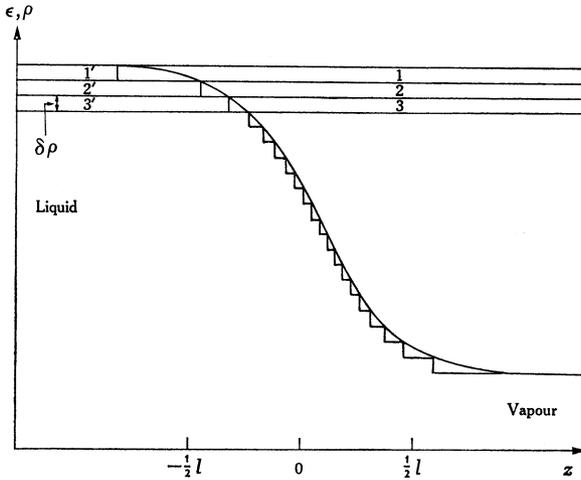


Fig. 4.—Model interface used to understand the meaning of van der Waals forces as calculated by Lifshitz theory.

Each cell i must have a width l_i which is much less than l but is large enough that the fluid in cell i may be considered to be a continuum. We suppose that the height $\delta\rho$ of each cell is the same for all cells, and consider virtual changes in l keeping $\delta\rho$ fixed.

Consider now a completely homogeneous liquid of density ρ . We may construct a liquid-gas system by rearranging the liquid from the right to the left in such a way as to create the given interface in Figure 4. The energy required to do this is the energy calculated by Lifshitz theory. We begin the process by removing the very top strip labelled 1 in Figure 4. We suppose that this requires an energy δE not including the actual self energy of the fluid. Now consider the removal of strip 2. If the strip 1' were not present in the liquid region, the energy required to remove strip 2 would be just δE again. However, we have also removed the van der Waals interactions between strip 1' and strip 2. Thus the total Lifshitz energy is the total van der Waals interaction energy removed by taking away the liquid in the gaseous region. The extra energy involved in this removal process is $n \delta E$ which is the energy of a sharp interface situated at $z = 0$. This $n \delta E$ term is not included in the calculations of the interface width because it is independent of l . Furthermore, the sharp interface is the standard state to which calculations of surface tension are referred (Cahn and Hilliard 1958). Thus it may not contribute to the surface tension either. The self energy term mentioned above is just that introduced into Section II.

