Surface tension and contact angles: molecular origins and associated microstructure

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Abstract

Gradient theory converts the molecular theory of inhomogeneous fluid into nonlinear boundary value problems for density and stress distributions in fluid interfaces, contact line regions, nuclei and microdroplets, and other fluid microstructures. The relationship between the basic patterns of fluid phase behavior and the occurrence and stability of fluid microstructures is clearly established by the theory. All the inputs of the theory have molecular expressions which are computable from simple models.

On another level, the theory becomes a phenomenological framework in which the equation of state of homogeneous fluid and sets of influence parameters of inhomogeneous fluids are the inputs and the structures, stress tensions and contact angles of menisci are the outputs—outputs that find applications in the science and technology of drops and bubbles.

Introduction

As witnessed by the papers presented at this colloquium, drops and bubbles, thin films and adsorbed layers, and contact angles are key actors in numerous natural and man-made processes. With our knowledge of and demands on these processes becoming more sophisticated, it is increasingly important to have a molecular level theory of structure and stress in interfaces. Although the formal statistical mechanical theory of inhomogeneous fluids at equilibrium has been developed rather extensively over the last two decades, the formal theory is presently intractable. Far more powerful is gradient theory, an approximation going back to Rayleigh and van der Waals which was rediscovered by Cahn and Hilliard and was recently put into modern form by Cercignani et al. and Yang et al. Successes in predicting the surface tension of polymer melts, hydrocarbons and their mixtures, and water prove that the theory is useful for real fluids. In this paper, I outline the elements of gradient theory and describe applications that my Minnesota colleagues and I have made of the theory to fluid-fluid interfaces, fluids at solid surfaces, and drops and bubbles.

Gradient theory of microstructured fluids

A fluid microstructure is an inhomogeneous region in a fluid in which component densities vary appreciably over molecular distances. Any fluid is, of course, inhomogeneous because of the presence of gravity. However, the inhomogeneities that result from gravity are so weak that component densities vary negligibly over molecular distances. Similarly, the inhomogeneities induced by ordinary centrifugal fields and by the temperature and composition gradients involved in the usual transport situations are very weak. If the component densities vary sufficiently little over molecular distances, then the thermodynamic functions can be approximated locally by the corresponding functions for homogeneous fluid at the local composition. In fluid microstructures the effect of the local component density variations must be accounted for in the local thermodynamic functions.

In the absence of external fields and density inhomogeneities, the Helmholtz free energy density is \( f_0 \). From intermolecular interactions species \( i \) and \( j \) give to \( f_0 \) a contribution of the order of \( a_{ij} n_i n_j \), \( n_i \) and \( n_j \) being component densities and \( a_{ij} \) a characteristic energy parameter. The factor \( 1/2 n_i n_j \) is a measure of the number of interacting pairs. If the fluid is inhomogeneous at position \( r \), then the number of interacting pairs in the vicinity of \( r \) should be corrected by some amount \( n_i n_j \). An estimate of \( n_i n_j \) is \( n_i n_j \) the range of the intermolecular force between \( i \) and \( j \) and \( n_i n_j \) the gradient of \( n_i \) at \( r \). It follows heuristically then that the local Helmholtz free energy density of inhomogeneous fluid is \( f_0(n) + \frac{1}{2} c_{ij} n_i n_j + \text{terms higher order in gradients of component densities; } f_0(n(r)) \) is the Helmholtz free energy density of homogeneous fluid at the local composition \( n(r) = (n_1(r), n_2(r), \ldots, n_i(r)) \) and the terms involving density gradients are the Helmholtz free energy density of the inhomogeneity. The quantity \( c_{ij} \) is proportional to \( a_{ij} r_{ij} \), the proportionality factor arising from appropriate molecular averaging. If an external conservative potential \( u(r) \) is present, then to the local free energy density is added \( \Sigma n_i u_i \). Putting together the pieces of this heuristic argument, one gets the gradient theoretical formula for the Helmholtz free energy \( F \) of inhomogeneous fluid.
\[
F = \int \left\{ f_0(n) + \sum_{i,j} \frac{1}{2} c_{ij} \mathbf{V} n_i \cdot \mathbf{V} n_j + \sum_{i} n_i \, d^3 \mathbf{r} \right\}.
\]

If the density gradients are macroscopic, e.g., caused by gravity or ordinary centrifugal fields, then \( \mathbf{V} n_i \) is of the order of \( n_i/L \), \( L \) being the dimension of the system. In this case the quantity \( c_{ij} \mathbf{V} n_i \cdot \mathbf{V} n_j \) is negligible since it is of the order of \( (\mathbf{r}_{ij}/L)^2 \) compared to the local value of the homogeneous fluid free energy density \( f_0 \). Thus, it is appropriate to identify \( \sum_{i,j} \frac{1}{2} c_{ij} \mathbf{V} n_i \cdot \mathbf{V} n_j \) as the free energy density of fluid microstructure.

Van der Waals introduced the one-component version of Equation (1) in his theory of liquid-vapor interfaces and Cahn and Hilliard used a binary regular solution version of the equation in connection with interfacial structure and spinodal decomposition of subcooled homogeneous solution. In the modern statistical mechanical version of the theory,10 Equation (1) is derived from a formal component density expansion of the exact free energy of inhomogeneous fluid. Expressions are obtained which relate the local "influence parameters" \( c_{ij} \) of inhomogeneous fluid to the fluid radial distribution functions of homogeneous fluid at local component densities. The heuristic connection of the influence parameter \( c_{ij} \) to \( a_{ij}r_{ij} \) is justified by the rigorous statistical mechanical expressions.

In its modern version gradient theory is a very attractive description of inhomogeneous fluid. On the one hand the inputs \( f_0(n) \) and \( c_{ij}(n) \) can in principle be computed from the molecular theory of homogeneous fluid, but on the other hand if molecular theory is insufficiently developed for the fluids of interest semiempirical or empirical schemes can be used to deduce equations of state for \( f_0(n) \) and \( c_{ij}(n) \). Along these lines it is encouraging that the molecular theoretical formulas for \( c_{ij} \) and some predictions12,13 based on simple models imply that the influence parameters are often only weak functions of component densities. Similarly, the success of the theory with constant \( c_{ij} \) in predicting the surface tensions of hydrocarbon mixtures18 and water19 argues against appreciable density dependence of the influence parameters. The importance of this is that one can determine the values of influence parameters from limited experimental data. In all the applications I discuss below the influence parameters are held constant.

At equilibrium the grand potential,

\[
\Omega = F - \sum_{i} \mu_i \int \mathbf{V} n_i \, d^3 \mathbf{r} ,
\]

is a minimum in a closed system. The chemical potential, \( \mu_i \), plays the role of a Lagrange multiplier accounting for the constraint that \( N_i = n_i d^3 \mathbf{r} \) is fixed in a closed system. The density distributions \( n_i(r) \), \( i=1,\ldots,v \), that minimize \( \Omega \) must, according to the calculus of variations, obey the corresponding Euler equations

\[
\mu_i = \mu_i^e + \mu_i^o(n) - \sum_j V^o(c_{ij} \mathbf{V} n_j) + \sum_{j,k} \frac{1}{2} \frac{\partial^2}{\partial n_k} \mathbf{V} n_j \cdot \mathbf{V} n_k \, \mu_k^o + \frac{3}{2} \beta c_{lk}^{lab}/n_k ,
\]

\( i=1,\ldots,v \). Boundary conditions appropriate for a given fluid microstructure must be assigned and the component densities of the microstructure determined by solving these nonlinear differential equations. Thus, gradient theory reduces the problem of determining equilibrium fluid microstructures to a nonlinear boundary value problem. Of course, once a microstructure solution has been obtained its stability has to be established by proving that it is a local minimum of the grand potential \( \Omega \). Typically one solves nonlinear differential equations by discretization (e.g., finite difference or finite element) and iteration using the Newton-Raphson technique.5 A biproduct of such a solution technique is that the matrix generated by the Newton-Raphson technique is the one required for stability analysis of the solution so obtained, i.e., the same algorithm generates the solution and the elements of stability analysis.

The pressure tensor is another quantity of interest in fluid microstructures. In homogeneous fluid, the pressure is isotropic, i.e., the number of lines of force passing through a small element of area from one side of the element to the other is independent of the orientation of the element. This is because the molecular population is identical in all directions in homogeneous fluid. This is not true in inhomogeneous fluid and so the isotropic pressure of homogeneous fluid, \( P_0(n) \), must be corrected to account for local component density variation. \( \mathbf{T} \) is the unit tensor. Since the number of lines of force passing through the area element will depend on orientation, components of the pressure tensor are in general different in an inhomogeneous fluid, i.e., the pressure tensor \( P \) is anisotropic. To second order in density gradients the general formula for the pressure tensor is of the form
\[
P = P_0(n)_j + \epsilon_{ij} \left[ \epsilon_{ij}^{(1)} n_i n_j + \epsilon_{ij}^{(2)} (\nabla n_i) (\nabla n_j) + \left[ \epsilon_{ij}^{(3)} n_i n_j + \epsilon_{ij}^{(4)} (\nabla n_i) (\nabla n_j) \right] \right],
\]

where \(\epsilon_{ij}^{(1)}, \ldots, \epsilon_{ij}^{(4)}\) are functions of the local composition \(n\). The one component version of Equation (5) was first proposed by Korteweg. The theoretical formulas for the \(\epsilon_{ij}^{(3)}\) are much more complicated than that for the influence parameters. Several simplified versions of the \(\epsilon_{ij}^{(3)}\) have been investigated. The simplest of these is obtained by assuming that the influence parameters are constant and that the \(\epsilon_{ij}^{(3)}\) must be consistent with the constancy. The result is

\[
P = P_0(n) - \frac{2}{3} \epsilon_{ij} \left[ c_{ij} n_i n_j - \frac{1}{2} (\nabla n_i) (\nabla n_j) + \frac{1}{2} [n_i n_j - \frac{1}{2} (\nabla n_i) (\nabla n_j)] I \right].
\]

Since \(P_0\) and \(P_0\) are related by the thermodynamic relation \(dP_0 = -d(\epsilon_{ij} V)\), at constant \(T, n_i, \ldots, n_i V\), the gradient theory of stress given by Equation (5) requires exactly the same inputs as the gradient theory of the free energy.

In what follows the influence parameters are always assumed to be constant and either the van der Waals (VDW) equation of state or one of its empirically modified successors, the Peng-Robinson (PR) equation, is used. Both equations can be summarized as

\[
P_0(n) = \frac{nkT}{1-nb} \frac{n^2a}{1+\psi[2nb-(nb)^2]}
\]

\(\psi=0\) in the VDW equation and \(\psi=1\) in the PR equation. \(a\) and \(b\) are energy and volume parameters. For pure fluids the parameters are determined by the critical temperature and pressure for the VDW equation and these plus the acentric factor for the PR equation. The recommended forms of \(a\) and \(b\) for mixtures is \(nb = \sum n_i b_i\) and \(n^2a = \sum n_i n_j a_{ij}\), where \(b_i\) and \(a_{ij}\) are pure fluid parameters and \(a_{ij}\) are mixture parameters that are determined by a fit of the equation to experimental data on two-component systems. The PR equation is quantitatively superior to the VDW equation but qualitatively both are quite similar, and so either serves equally well the purposes of this article.

**Planar interfaces**

The component density profiles, \(n_i(x)\), of a planar interface are obtained by solving Equation (3) with \(u_i = 0\) and subject to the boundary conditions \(n(x = -\infty) = n^{(1)}\) and \(n(x = \infty) = n^{(2)}\), where \(n^{(1)}\) and \(n^{(2)}\) denote the component densities in coexisting bulk phases 1 and 2. These component densities are of course determined by the usual equilibrium conditions \(P_{eq}(n^{(1)}) = P_{eq}(n^{(2)})\), \(u_i^{(1)}(n^{(1)}) = u_i^{(2)}(n^{(2)})\), \(i=1,\ldots,\nu\). Equation (3) can be solved analytically in the case of a one-component fluid but must be solved numerically in the multicomponent case.

The density profile of a one-component liquid-vapor interface predicted with the VDW equation at the reduced temperature \(kTb/a = 0.197\) is shown in Figure 1. The density is

Figure 1. Density in units of \(b^{-1}\), distance in \(c/a\). \(kTb/a = 0.197\). Ref. 14.
given in units of $b^{-1}$ and the distance in units of $v/c/a$, a length of the order of magnitude of a molecular diameter. In a planar interface the normal pressure $P_N$, that is the component of pressure measured by a flat test surface lying in the interfacial plane, is constant in accordance with the condition of hydrostatic equilibrium ($\nabla \cdot P = 0$, or $dP_N/dx = 0$ since $P = P_N + P_T(j_j + k_k)$, $i$ the unit vector along the x-axis). On the other hand, the transverse pressure $P_T$, the component of pressure measured by a flat test surface orthogonal to the interfacial plane, is not constrained by hydrostatic equilibrium and must take on whatever values forced on it by the density profile. $P_T$ cannot be constant in the interface; otherwise, the interfacial tension, which is the difference between the normal and transverse pressures integrated across the interface, namely,

$$\gamma = \int_{-\infty}^{\infty} (P_N - P_T)dx,$$

would have to be zero.

From Equation (5) it follows that

$$P_T = \frac{2}{3} P_0(n) + \frac{1}{3} P_N,$$  \hspace{1cm} (8)

This result, which has been derived from several approximations to the coefficients in the gradient theoretical pressure tensor, is heuristically very suggestive. The density $n(x)$ is uniform in a plane parallel to the interface, that is the pressure is isotropic in such a plane. The contribution to the transverse pressure from molecules lying near the plane is expected to be proportional to $P_0(n(x))$. Molecules lying further from the plane are distributed to maintain a constant normal pressure $P_N$. The contribution of the so-distributed molecules to the transverse pressure should be of same order of magnitude. Thus, it might be argued that $P_T$ will be a linear combination of $P_0(n)$ and $P_N$, the respective coefficients being 2/3 and 1/3 reflecting the fact that the dimensions of the interfacial plane are 2 and the normal direction is 1. It would be interesting to find a convincing derivation of Equation (8) from this point of view. An accounting of the lines of intermolecular force passing through a small element of area versus orientation of the element might be fruitful in pursuing this goal.

An important implication of Equation (8) is that the structure of the transverse pressure in the interface is determined by the equation of state of homogeneous fluid. The normal and transverse pressures corresponding to the profile in Figure 1 are shown in Figure 2. As expected there is a wide region in which the interface is under tension (i.e., $P_T < P_N$). Since tension is positive and equals the area under the curve $P_N - P_T$ versus $x$, there must be a region in which $P_T > P_N$. There is however a small region of compression ($P_T > P_N$) on the gas side of the interface. The correspondence between the van der Waals loops in the PVT phase diagram for homogeneous fluid is seen by comparing Figures 2 and 3. The normal pressure $P_N$ is of course the liquid-vapor coexistence pressure, i.e., $P_N = P_0(n_0(n)) = P_0(n_v(n))$, $n_l$ and $n_v$ the liquid and vapor densities, respectively. The region of compression in the interface arises from the region in which the pressure isotherms lies above the tie-lines, which locate the pressure $P_N$.

A significant feature of the theory is that the structure and stress in the interface are determined by the thermodynamic functions of homogeneous fluid in the metastable and unstable regions of the PVT diagram. It has usually been thought that in the unstable region of the phase diagram the thermodynamic functions are meaningless. Far from being meaningless, the behavior of these functions in this region is a determining factor of interfacial behavior. The gradient terms provide the necessary free energy to stabilize states that would be unstable in homogeneous fluid.

As a critical point or a solution plait point is approached, the VDW loops in the pressure isotherm begin to flatten out and become symmetric about the tie-line, both patterns of which drive the tension towards zero. That tension goes to zero as a critical point is approached is well-known, but the mechanism of getting low tension by symmetrizing the VDW loops of the pressure isotherm is novel. Such an example is provided in Figure 4, in which is given density and pressure profiles of the liquid-liquid interface of carbon dioxide and decane. The profiles were predicted with the PR equation using the mixture parameter values $a_{12} = 0.1 a_{11} a_{22}$ and $c_{12} = 0.9 c_{11} c_{22}$ and $c_{11}$ surface tension. The tension of the interface in Figure 4 is $\gamma = 0.6 \text{ dyn/cm}$. 

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Figure 2. Principal pressures in a planar interface. VDW fluid. Pressure in units of $a/b^2$, distance in $\xi C/a$. Ref. 14.

Figure 3. PVT phase diagram of a VDW fluid. Density in units of $b^{-1}$, temperature in $a/k_b$. The liquid-vapor densities are indicated by points connected with constant-pressure tie-lines.

Figure 4. Density and principal pressure profiles of a CO$_2$-decane liquid-liquid interface of a PR fluid. $kTb/a = 0.148$, density $n_i$ in units of $b^{-1}$, distance in $\xi C/a$, pressure in $a/b^2$. $a$, $b$, $c$ CO$_2$ values. Ref. 19.
Contact angle, wettability, and film formation

The adsorption and wetting characteristics of fluids on solid surfaces and at fluid-fluid interfaces are of enormous practical interest in the design of detergents, lubricants, flotation and foaming agents, paints, capillary delivery devices, and the like. In spite of such practical importance, the molecular theory of adsorption and wetting is still a fledgling science, based most often on ad hoc models for various special situations. Gradient theory shows promise of giving a unified theoretical basis to the subject. In what follows, the theory is applied to adsorption and film formation at interfaces, three phase contact regions and the contact angle, and perfect wetting transitions.

Suppose a fluid-fluid interface contacts a flat solid wall as indicated in Figure 5. If the meniscus (a mathematical surface representing the position of the interface) is observed at some distance R lying far enough from the solid for bulk fluid phases to exist on each side of the surface but not far enough for gravitational distortion to affect it, then the observed contact angle \( \theta \) obeys Young's equation

\[
\gamma_{\gamma a} = \gamma_{\gamma b} + \gamma_{ab} \cos \theta .
\]  

(9)

\( \gamma_{\gamma a} \) and \( \gamma_{\gamma b} \) denote the tensions (or surface excess free energies) of fluid phases a and b with solid phase \( \gamma \). \( \gamma_{ab} \) is the interfacial tension of the interface between fluids a and b. The basis and meaning of Equation (9), which can be derived from a force balance on the hemicylinder whose cross-section is shown in dashed lines in Figure 5, has been discussed at length in a recent paper by Benner et al.\(^\text{15}\)

If all three phase are fluid, then the menisci define three dihedral angles (Figure 6) obeying the force balance

\[
\frac{\gamma_{ab}}{\sin \gamma} = \frac{\gamma_{\gamma b}}{\sin \alpha} = \frac{\gamma_{\gamma a}}{\sin \beta} .
\]  

(10)

A contact angle is not always observed when three phases are brought together. If either of the inequalities

\[
\gamma_{\gamma a} > \gamma_{\gamma b} + \gamma_{ab} \quad \text{or} \quad \gamma_{\gamma b} > \gamma_{\gamma a} + \gamma_{ab}
\]  

(11)

then Equation (9) (or (10)) has no solution and the free energy of the system will decrease as the result of a thin layer of phase b (or phase a) intruding between phase \( \gamma \) and phase a (or b) as shown in Figure 7. The intruding phase is said to completely or perfectly wet the interface between the other two phases. The transition between contact angle and perfect wetting behavior occurs at conditions for which one of the inequalities in Equation (11) becomes an equality.
Perfect wetting is of course essential in applications involving spontaneous spreading of some fluid at an interface. Examples of perfect wetting are well-known. In the presence of air, most liquids perfectly wet on clean metal surfaces, water on quartz, some organic liquids on water, some organic liquids on some polymers, etc. Not so well-known is critical point wetting, a phenomenon hypothesized recently by Cahn. He noted that according to critical point theory and experiment, as a critical point of phase α and β is approached along a temperature, pressure, or chemical potential path, the interfacial tension approaches zero asymptotically as

\[ \gamma_{\alpha\beta} = \gamma_{\alpha\beta}^0 \left| 1 - \frac{h}{h_c} \right|^{1.3}, \]  

where \( h \) is the field variable (any thermodynamic quantity being the same in all coexisting phases), \( h_c \) its value at the critical point, and \( \gamma_{\alpha\beta}^0 \) a scale factor. Cahn postulated that the difference \( \gamma_{\alpha\beta} - \gamma_{\alpha\beta}^0 \) will approach zero as the composition of the components in phases α and β approach each other, i.e., it obeys the scaling law

\[ \left| \gamma_{\alpha\beta} - \gamma_{\alpha\beta}^0 \right| = \gamma_{\alpha\beta}^0 \left| 1 - \frac{h}{h_c} \right|^{0.34} \]  

sufficiently near the critical point. Since \( \gamma_{\alpha\beta}^0 \) approaches zero faster than that postulated for \( \gamma_{\alpha\beta} - \gamma_{\alpha\beta}^0 \), Cahn concluded that there will always exist a critical wetting value of the field variable, \( h_{cw} \), at which one of the fluids will become perfectly wetting. The combination of Equations (9), (12) and (13) gives asymptotic formulas for the contact angle at a solid as \( h \) approaches \( h_{cw} \), namely,

\[ \cos \theta = \frac{\gamma_{\alpha\beta}^0}{h_{cw} - h_{cw}} \left| 1 - \frac{h}{h_c} \right|^{0.96} \]  

where \( \gamma_{\alpha\beta}^0 \) is the value of \( \gamma_{\alpha\beta} \) at \( h = h_{cw} \).

The practical significance of Cahn's theory is that one of a pair of fluids can always be made perfectly wetting in the presence in a third phase by adjusting field variables (e.g., by changing temperature or pressure or by adding some component) to get near a critical point.

To test the validity of Equation (13), an unverified hypothesis, and to understand the relation of \( h_{cw} \) and \( h_{cw} \) to fluid and solid properties and interfacial structure, Teletzke et al. studied with gradient theory the behavior of a one-component fluid at a flat solid wall. Some results of this work are of interest here. The PR equation of state was used for the fluid and the wall was characterized by the wall-fluid molecule potential.

\[ u(x) = W \left[ \frac{1}{d_1} \left( \frac{d_2}{x} \right)^9 - \frac{1}{d_6} \left( \frac{d_3}{x} \right)^3 \right], \]  

where \( W \) is a measure of the strength of the wall-fluid potential and \( d \) its range.

A PR fluid has an upper critical temperature \( T_c \) equal to 0.1704 in the units \( a/b \).
Gradient theory predicts a critical-wetting temperature $T_{cw}$ above which the liquid phase becomes perfectly wetting at the solid-vapor surface. An example is shown in Figure 8, for the solid-fluid parameters $W = 6.4 a/b$ and $d = \sqrt{c/a}$. Below $T_{cw}$, a drop of liquid would not spread on the solid, but would form a contact angle. Above $T_{cw}$, the drop would spread to form a perfectly wetting layer. The critical wetting temperature depends on $W$ and $d$. At fixed $d$, $T_{cw}$ decreases with increasing $W$, i.e., as the strength of the solid-liquid potential increases perfect wetting occurs at lower temperature. At fixed $W$, $T_{cw}$ decreases with increasing range $d$ of the wall potential, i.e., the longer the range of the potential the lower the temperature at which perfect wetting occurs.

Correspondingly, the characteristic tension $\gamma_c \equiv \gamma_{LV}(T_{cw})$ decreases with increasing $T_{cw}$ (and, therefore, with decreasing $W$ or $d$). If $W$ and/or $d$ are small enough, then $T_{cw}$ is near the critical point and Equation (14) should hold if Cahn's hypothesis is true. This was indeed found to be true (although there is a small detail of mean-field versus correct scaling laws[21]). On the other hand, as $W$ and/or $d$ increase, the perfect-wetting temperature $T_{cw}$ decreases and Equation (14) no longer holds. At sufficiently low temperature the interface is very sharp (narrow) and the Good-Girifalco formula:

$$\cos \theta = 2 \frac{\gamma_c}{\gamma_{LV}} - 1$$

ought to hold since it is based on a discontinuous interface approximation. This turns out to be the case. The dependence of $T_{cw}$ and $\gamma_c = \gamma_{LV}(T_{cw})$ on $W$ and the dependence of $\cos \theta$ on $\gamma_{LV}(T)/\gamma_c$ for various values of $W$ are shown in Figures 9 and 10 for the case $d = \sqrt{c/a}$. The
near-critical scaling law, Equation (14), holds for $W < 3$, the Good-Girifalco formula, Equation (16), holds for $W > 9$. In the intermediate range, neither formula holds.

Several years ago, Zisman suggested that the contact angle correlates with the ratio $\gamma_l \gamma_s / \gamma_{ls}$ but that $\gamma_{ls}$ was a characteristic only of the solid, not of the fluid phase. The implication of Figure 9 is that this is not so unless the reduced energy parameters $W/\alpha$ and length parameter $\delta / \sqrt{\gamma / \alpha}$ are fixed in the series of fluids compared. As these ratios depend both on solid and fluid, it appears that Zisman's scaling worked because the fluid parameters $\beta / \alpha$ and $\sqrt{\gamma / \alpha}$ were not very different for the systems compared.

Another thing gradient theory predicts is a first order transition of the absorbed layer at the solid surface. In the temperature range $T_{cw}$ to $T_{cs}$ (Figure 8), as the bulk fluid density increases from zero towards the gas side of the phase diagram a composition is reached at which two adsorbed layers or thin-films of different thickness are predicted at the same equilibrium conditions. An example is shown in Figure 11. As the bulk density is increased beyond the thin-film coexistence curve the thin-film grows continuously into a thick film to become finally a perfectly wetting layer of liquid when the liquid-vapor phase dome is reached. The temperature $T_{cs}$ is a film critical point. Above $T_{cs}$, as bulk density increases from zero to the liquid-vapor coexistence curve an adsorbed layer grows continuously through thin-film states into a perfectly wetting layer of liquid phase. Below $T_{cw}$ only submonolayer adsorption occurs with increasing density until at the liquid-vapor coexistence curve liquid appears as a drop with a contact angle. On the liquid side of the coexistence region only submonolayer adsorption occurs. A thin-film transition was predicted by Samm and Ebner using an integral model free energy. Their thin-film coexistence curve is very similar to that of described here. The thin-film transition predicted by Cahn on the basis of a two-dimensional model of the solid is, however, qualitatively different.21

It should be emphasized that according to the theory the patterns of film and phase behavior of a one-component fluid at a solid wall are general. Sufficiently near a critical point of a pair $\alpha$ and $\beta$ of multicomponent coexisting fluid phases, either $\alpha$ or $\beta$ will become perfectly wetting at the interface formed by a third phase $\gamma$ and the nonwetting fluid phase. The third phase $\gamma$ can be solid or liquid. The critical point can be an upper or lower critical point. In approaching a critical point along any field variable, e.g., temperature, pressure, or chemical potential of a component, there will be a critical wetting value $h_{cw}$, a finite distance from the critical point value $h_{crit}$ at which one of the near-critical phases becomes perfectly wetting on a third phase. Outside but near the coexistence composition region of $\alpha$ and $\beta$, a first order thin-film transition occurs with a coexistence curve lying between $h_{cw}$ and $h_{cs}$, $h_{cs}$ being the film critical point. $h_{cs}$ lies between $h_{cw}$ and $h_{cr}$. If $h$ lies between $h_{cw}$ and $h_{cr}$, then sufficiently near the $\alpha$-$\beta$ coexistence region a thin-film formed between the third phase $\gamma$ and, say, phase $\alpha$ will thicken continuously into a layer of the perfectly wetting phase $\beta$.

An example of the structure and stress of a liquid-vapor interface at which a thin film has almost grown into a layer of a second liquid phase is shown in Figure 12. This figure was taken from the work of Falls et al. in which theory was applied with the PR equation to planar interfaces and spherical drops formed in carbon dioxide and decane mixtures. The transverse pressure profile is highly structured, looking like that of a liquid-liquid interface on the left and of a liquid-vapor interface on the right.

There is abundant evidence that the qualitative patterns of wetting transitions described here are correct and the expected continuously thickening thin films have been observed by ellipsometry. However, the predicted first order thin-film transition has not been verified experimentally, nor have the critical exponents of Equations (13) and (14) been established experimentally.

The theory of wetting transitions and film formation at flat surfaces requires solving only a one-dimensional density profile problem. However, if the structure and stress of
Figure 12. Density and pressure profiles of a thin-film LC a liquid-vapor interface in CO₂ and decane. Density $n_4$ in units $b_1^3$, distance in $\sqrt{c_{11}/a_{11}}$ and pressure in $a_{11}/b_1$. Component 1 is CO₂.

$kTb_1/a_{11} = 0.148$. Ref. 19.

the three phase contact region is desired, the problem becomes of necessity greater than one-dimensional, even if one phase is a flat solid. If a fluid-fluid interface contacts a flat solid the component densities depend on the distance $x$ from the wall and the distance $y$ parallel to the wall. Benner et al. have recently studied the contact region of a one-component liquid-vapor interface at flat solid. The PR equation was used for the fluid and Equation (15) for the wall-fluid interaction potential. The space available here does not allow an extensive discussion of the paper. However, one interesting feature is that the stress state in the liquid-vapor interface is affected relatively far from the interface. An example of this is given in Figure 13. The principal pressure directions in the $x$-$y$ plane are indicated by crosses, the size of which indicates the magnitudes of the principal pressures in the $x$-$y$ plane. Far away from the solid and the liquid-vapor meniscus (defined as the position where $n(x,y) = 1/2(n_a + n_2)$ and indicated by the solid curve) the pressure components equal the bulk fluid value which is so small the corresponding crosses are almost invisible on the scale of Figure 13. At a planar liquid-vapor interface the normal pressure component ($P_{11}$) would be constant and therefore the pressure crosses would appear as horizontal lines ($P_{22}$ large, $P_{11}$ small) in the interfacial zone. Instead, even to the far right of Figure 13, a distance of about 25 molecular diameters away from the wall, the normal pressure component is very large. And the principal stress pairs $P_{11}$, $P_{22}$ undergo four sign changes in going from the liquid to the vapor phase. Wild and wonderful patterns! Are they consequential? A major conclusion from the work of Benner et al. is that at a flat surface Young's equation is applicable outside the contact region (see Figure 5). The radius of the contact region is $0.1W = 25a$, Width of region shown is $25a/6$, $P_{11}$, $P_{22} > 0$. Ref. 15.
Spherical fluid microstructures

Visible examples of spherical microstructures are the drops and bubbles that occur in mists, foams, beverages, manufactured glass, and basalt lavas. Invisible examples are colloidal particles, vesicles, and micelles. The classical description of spherical structures is based on the Young-Laplace equation and the Kelvin equation expressing mechanical and chemical equilibrium between a bulk phase interior and a bulk phase exterior separated by an interface having the tension of a planar interface. In a sufficiently small spherical microstructure, however, the interior will not be bulk phase and the tension will not be that of a planar interface. Deviation from classical behavior might be consequential in nucleating fluids and micellar solutions, in which the equilibrium microstructures are tens of angstroms in diameter and, to mention a couple of examples receiving special attention at this colloquium, microdrops or microbubbles in microdrops and thin liquid layers on the inside of glass shells.

Gradient theory provides a molecular level theory of spherical structures which establishes the point at which the classical description breaks down and determines the structure, stress and mechanisms of stability of spherical microstructures. By way of example, I will outline some results of the recent investigations of Falls et al. on one and two-component microdrops and microbubbles.

For spherical microstructures suspended in bulk fluid, the boundary conditions are \( \frac{\partial n_i}{\partial r} = 0 \) at \( r=0 \) and \( n_i(r) = n_{iB} \) as \( r \to \infty \), \( n_{iB} \) being the bulk phase density of \( i \) in the suspending fluid. With these boundary conditions and constant influence parameters, Falls et al. have solved gradient theory for a one-component VDW fluid and a two-component PR fluid. Figure 14 illustrates their results for the density profiles \( n(r) \) of liquid-like microdrops suspended in a vapor phase. From the Young-Laplace and Kelvin equations, one expects the interior of the drop to be at higher pressure, and therefore higher density, than the saturated liquid density \( n_B \). This is seen to be true in Figure 14 for drops of radius larger than about four molecular diameters (the "radius" of the drop does not have a precise meaning for microdrops). However, for smaller drops, the interior density decreases with drop size and the density profile takes on a Gaussian-like shape with no interior bulk region. The loss of a bulk-like interior begins to occur when the radius of the drop is about equal to the thickness of the liquid vapor interface.

Because the interface is curved, the normal pressure profile \( P_n \) \( (P = P_N(r) + P_T(r)) \) in a spherical fluid structure is not constant across the interface. Thus, the pressure profiles in a spherical interface are quite different from those in a planar interface at the same temperature (compare Figures 15 and 12). This leads one to expect strong deviations between the tension \( \gamma \) of a planar interface and the tension \( \gamma(R) \) of a microdrop of radius \( R \). Similar deviations are expected for the Young-Laplace equation as classically applied. From the thermodynamics of drops it follows that the appropriate radius \( R \) with which to describe the tension of the drop is the radius of the surface of tension. This radius, which does not differ greatly from the value of \( r \) at which \( n(r) = 1/2 \) \( n(r=0) + n_B \) and the corresponding tension \( \gamma(R) \) are predicted by gradient theory. As illustrated in Table 1, the tension of the drop does differ from \( \gamma \) for small drops and the classical Young-Laplace equation does break down. However, what is remarkable is that already for drops fifteen molecules wide the drop interface has virtually the same tension as a planar interface and the classical Young-Laplace equation is accurate.
Table 1. Microdrops in VDW vapor. Radius $R$ in units of $\sqrt{c/a}$. $kTb/a = 0.197$.  

<table>
<thead>
<tr>
<th>$R$</th>
<th>$\gamma(R)/\gamma_0$</th>
<th>$F_R(0) - F_R(\infty)$</th>
<th>$(2\gamma_0/R)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.56</td>
<td>0.79</td>
<td>-0.079</td>
<td></td>
</tr>
<tr>
<td>2.88</td>
<td>0.83</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>3.26</td>
<td>0.87</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>3.76</td>
<td>0.91</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>4.67</td>
<td>0.95</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>5.52</td>
<td>0.97</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>7.74</td>
<td>0.99</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>10.15</td>
<td>0.996</td>
<td>0.99</td>
<td></td>
</tr>
</tbody>
</table>

Figure 15. Principal pressure profiles of a microspherical drop in a VDW vapor. Pressure in units of $a/b^2$, density in $b^2$, distance in $c/a$. $kTb/a = 0.197$. Ref. 14.

The implication of the one-component studies just outlined is that microdrop curvature affects the interfacial structure and the interfacial tension very little once the drop radius is larger than 10 molecular diameters. In multicomponent systems this conclusion may or may not follow. Consider for example the bubble in liquid CO$_2$ and decane shown in Figure 16 (from Falls et al.). The radius of the bubble is only about 12 carbon dioxide diameters, but its component density profiles are almost identical to those of the planar liquid vapor interface (indicated as a bubble with $R\infty$).

Figure 16. Density profiles in a planar liquid-vapor interface ($R\infty$) and in a bubble ($R = 12$) in a CO$_2$-decane FR fluid. Density $n$, in units of $b^2$, distance in $c/a$. $kTb/a = 0.148$. Ref. 19.
The tensions of the bubble and planar interface agree within 10%. Thus, this bubble behaves as expected from the one-component results.

However, as was discussed in the previous section (Figure 12), in a multicomponent fluid conditions can be such that a thin-film of an incipient third phase may be formed at an interface. These films are very sensitive to a change in a field variable. Curving an interface changes the chemical potential of the system (this follows from Kelvin's equation in the classical theory), and so it can be anticipated that under conditions of high adsorption or thin-film formation the interfacial structure and stress will be very sensitive to drop size. Comparison of the drop component density and pressure profiles of Figure 17 (from Falls et al.13) with the corresponding planar case, Figure 12, illustrates that this is indeed the case. At this temperature, it has been estimated19 from the theory that the drop structure will not begin take on the planar form until it is larger than 100 carbon dioxide molecules in radius. The important implication of this result is that in regions of thin-film formation the interfacial composition can be greatly modified by curvature. This fact might be quite important in the manufacture of objects with thin, uniform layers of a desired material.

Although space does not allow discussion, gradient theory predicts the work of formation of drops and bubbles, a quantity important to the theory of homogeneous nucleation. In fact, the theory was used by Cahn11 to support his theory of spinodal decomposition. He showed that the barrier expected for the nucleation of microdrops is not there owing to the size dependence of the interfacial tension and that as a result a homogeneous material at the spinodal density can transform continuously into a multiphase system. In heterogeneous nucleation, it is likely that thin-film formation will be an important intermediate step in the process when conditions are right. These matters are ripe for future work.

Closing remarks

In closing, I would like to point out a few problems to which gradient theory might profitably be applied next.
1. Thin, uniform layers of fluid in a spherical solid shell. A fluid-solid potential will have to be introduced for shell. For uniform thin-films and thin layers of phase only spherically symmetric solutions need to be sought, so the problem remains one dimensional. By a different method Kim, Hock, and Bernat address this problem in their paper.
2. Fluid microstructure at rough or chemically heterogeneous solid surfaces. For this problem a two-dimensional solid-fluid potential will have to be introduced. Thus, the problem is two-dimensional.
3. Contact angles with rough or chemically heterogeneous solid surfaces. This involves the same solid-fluid potential as in Problem 2 and a fluid interface in the vicinity of

![Figure 17. Density and pressure profiles of a drop in a CO2-decane PR fluid. Density $n_i$ in units of $kT/b_i^2$, pressure in $a_{11}/b_i$, distance in $\sqrt{a_{11}/2}$, $kTb_i/a_{11} = 0.148$. Ref. 19.](image)
the solid and so is a three-dimensional problem. The problem will pose a challenge to
computer-aided mathematics.

4. Drop shapes on inclined rough or chemically heterogeneous surfaces. This again is
a three-dimensional problem and an even greater challenge than Problem 3.

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