From: R. Lipowsky: **Critical Behavior of Interfaces: Wetting, Surface Melting, and Related Phenomena**;
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II. THREE PHASES IN CONTACT

A. Complete versus incomplete wetting

Consider an inhomogeneous system with two coexisting phases, α and γ, as shown in Fig. 1(a). Usually, the interface between the two phases has a microscopic width. If α and γ are two fluid phases, this width is of the order of the bulk correlation lengths within the phases α and γ. If α is a liquid and γ a solid, the density profile of the liquid exhibits density oscillations on a scale which is set by the size of the molecules. Typically, these oscillations are confined to a few interatomic spacings from the solid wall.

Now, let us change a thermodynamic field, e.g., temperature or pressure, in such a way that the system approaches a triple point where a third phase, β, can coexist with the two phases α and γ. Then, in thermal equilibrium, a layer of the β phase may appear in the $\alpha\gamma$ interface. As one comes closer and closer to the triple point, the thickness of this intermediate layer may continuously grow: this is the case of *complete wetting*. On the other hand, no layer may appear in the $\alpha\gamma$ interface or the thickness of this layer may saturate and remain finite as the triple point is attained: this is the case of *incomplete wetting*.

In real systems which have a finite size, the thickness of the β layer cannot become arbitrarily large even in the case of complete wetting. Nevertheless, one can usually distinguish complete and incomplete wetting even in a finite system via the behavior of the $\alpha\gamma$ interface at the triple point. First, consider an $\alpha\gamma$ interface which is incompletely wet by the β phase. Then, at the triple point, further addition of β phase into the $\alpha\gamma$ interface will lead to the formation of *droplets* with a finite contact angle, compare Fig. 1(b). In such a situation, the interfacial tensions, Σ, between the three phases satisfy the inequality (e.g., Landau and Lifshitz, 1970; Rowlinson and Widom, 1982)

$$\Sigma_{\alpha\gamma} < \Sigma_{\alpha\beta} + \Sigma_{\beta\gamma} \quad . \qquad (2.1)$$

This follows directly from a balance of the interfacial tensions at the point where the three interfaces meet. On the other hand, if the $\alpha\gamma$ interface is completely wet by the β phase, further addition of the β phase at the triple point leads to a continuous thickening of the β layer, see Fig. 1(c) . In this case, the contact angle vanishes and the interfacial tensions satisfy "Antonoff's rule"

$$\Sigma_{\alpha\gamma} = \Sigma_{\alpha\beta} + \Sigma_{\beta\gamma} \quad . \qquad (2.2)$$

One should note that, in thermal equilibrium, $\Sigma_{\alpha\gamma}$ *cannot be larger than* $\Sigma_{\alpha\beta} + \Sigma_{\beta\gamma}$ (Widom, 1975). Indeed, if $\Sigma_{\alpha\gamma}$ were larger than $\Sigma_{\alpha\beta} + \Sigma_{\beta\gamma}$, the system could always lower its free energy by the formation of a β layer within the $\alpha\gamma$ interface which leads back to the state for which (2.2) is valid.

Typical values for interfacial tensions are $\Sigma \simeq 10 - 10^2$ erg/cm^2. Especially large tensions $\Sigma \simeq 10^3$ /cn^2 are observed for liquid metal - vapor interfaces and for the surfaces of 'hard' solids. Naively, one might expect that the relation

(2.2) is more likely to hold if $\Sigma_{\alpha\beta}$ or $\Sigma_{\beta\gamma}$ are *small*. Small tensions occur (i) near a bulk critical point, where two of the three phases become identical, and (ii) in the presence of surfactant molecules which can lower the tension by several orders of magnitude. Indeed, it has been predicted that complete wetting will usually occur close to a bulk critical point (Cahn, 1977) or a bulk tricritical point (Widom,1975). On the other hand, the effect of surfactant is more complex and has been found to depend on the chain length of the molecules: small and large amphiphilic molecules lead to complete and incomplete wetting, respectively (Borzi et al, 1986).

B. Examples

1. Three fluid phases

In the previous section, the three phases α,β and γ were assumed to be in thermal equilibrium. Such a situation has been studied experimentally near triple points of fluid phases. Two examples for such systems are: (i) Mixtures of water, oil, surfactant and cosurfactant. In this case wetting layers of a microemulsion phase, β, have been observed which intrude into the interface between a water-rich and an oil-rich phase (e.g., Lang et al, 1976); (ii) Binary liquid mixtures in coexistence with their vapor. Here, wetting layers of the high-density liquid phase, β, can appear in the interface of the low-density liquid phase and the vapor (e.g., Moldover and Cahn, 1980; O`D. Kwon et al, 1982; Schmidt and Moldover, 1983). The theoretical aspects of these experiments have been reviewed by Rowlinson and Widom (1982), and Sullivan and Telo da Gama (1986).

2. Adsorption and Wetting of a Container Wall

In many physical systems where wetting has been studied, two of the three phases represent different states of the same material while the third phase is an inert "spectator" phase consisting of a different material. First, consider the case where the spectator phase is a solid substrate or a container wall. This happens in the following three examples: (i) A gas of adatoms or molecules is adsorbed onto a solid substrate which leads to a formation of a thin liquid layer (e.g., Anderson and Sabisky, 1970; Krim et al, 1984; Findenegg and Löring, 1984; Bartosch and Gregory, 1985). The theoretical work on adsorption has been reviewed in Pandit et al (1982) and by Hauge (1985); (ii) A binary mixture is in contact with a container wall which prefers one of the two liquid phases (e.g., Pohl and Goldburg, 1982; Wu et al, 1986); and (iii) The isotropic liquid phase of a nematic liquid crystal is bounded by a wall which induces the nematic order near the wall (e.g., Yokoyama et al, 1983; Iimura et al, 1984; Hsiung et al, 1986). Such a wall-induced layer of the nematic phase was theoretically predicted by Sheng (1982).

3. Surface-induced Order/Disorder and Surface Melting

In the previous examples, wetting layers were formed on solid substrates or walls which play the role of an intert spectator phase. Similar effects can occur if the spectator phase, γ, is an inert gas (or the vacuum), i.e., near the *free surface* of a condensed phase, α. Indeed, it has been theoretically predicted that the free surface can induce a layer of β phase which is either more disordered or more ordered than the bulk phase, α (Lipowsky, 1982a, 1982b, 1984a, 1986a).

Surface-induced *disorder* has been observed (1) near the order-disorder transition of the binary alloy Cu_3Au (Sundaram et al, 1973; McRae and Malic, 1984; Alvarado et al, 1986; Buck and McRae, 1986), and (2) in experiments on surface melting near the bulk triple point of Pb (Frenken and van der Veen, 1985; Frenken, 1986) and of Ar (Zhu and Dash, 1986). The idea of surface-induced melting has a long history. A recent review is by Cahn (1986).

Surface-induced *order* has been observed near the nematic-isotropic transition (e.g., Beaglehole, 1982; Iimura et al, 1984) and near the smectic A-isotropic transition (e.g., Ocko et al, 1986) of several liquid crystals.

4. Disorder Induced by Domain Boundaries

A disordered phase may also be induced by internal surfaces such as domain boundaries. For example, near the melting temperature of a crystal, the disordered, liquid-like phase may appear in the grain-boundaries of the crystal. Such grain boundary melting has been observed in various computer simulations (e.g., Broughton and Gilmer, 1986). The appearance of a disordered phase has also been observed experimentally for *antiphase domain boundaries* of the binary alloy Ni_3Al (Cahn et al, 1986).

In the above examples, the two phases α and γ represent the same thermodynamic state and differ only in their crystalline orientation or in the orientation of their superlattices. This implies that the thickness of the disordered layer is finite as a result of the van der Waals forces between the molecules (Lipowsky, 1986b).

5. Two-dimensional systems

The physical systems mentioned so far are 3-dimensional. Wetting phenomena can also occur in systems with spatial dimensionality $d=2$ such as adsorbed monolayers. Indeed, many theoretical studies have been devoted to 2-dimensional systems (e.g., Abraham, 1980; Kroll and Lipowsky, 1983a; Huse and Fisher, 1984; Fisher, 1984). The theoretical predictions have been confirmed by computer simulations (e.g., Selke, 1984).

C. Simplified description: Two phases in a semi-infinite geometry

The examples discussed above are summarized in Table I. The inert spectator phase is indicated by (Sp). This phase, say γ, does not equilibrate with the α and β phase on the timescale of a typical experiment. Then, the presence of the spectator phase has two consequences: (i) it provides a geometric boundary such as a wall or surface for the phases α and β, and (ii) it exerts an external field on the molecules in the α and β phase. Consider, for example, the case of adsorption. Here, the gas of adatoms is confined to a half space by the presence of the solid substrate. Then, wetting by a liquid or a solid layer occurs as the pressure of the gas is increased towards the liquid-vapor or the solid-vapor coexistence curve of the adatoms, respectively. Similarly, for surface-induced disorder in a binary alloy, one may ignore the presence of the vapor (or vacuum) and describe the system by a semi-infinite crystal near a first-order bulk transition. In the latter example, the external field exerted by the spectator phase can be neglected since the magnitude of this field is proportional to the particle density in the spectator phase.

Thus, in the presence of a planar boundary such as a solid substrate or a free surface, wetting phenomena can occur near any locus of *two*-phase coexistence. From a theoretical point of view, this represents a useful simplification since it involves a smaller number of thermodynamic fields. Indeed, most microscopic models for wetting phenomena which have been studied theoretically are simple lattice models (e.g., De Olivera and Griffiths, 1978; Pandit et al, 1982; Lipowsky, 1982a) and Landau theories (e.g. Cahn, 1977; Sullivan, 1981; Pandit and Wortis, 1982; Nakanishi and Fisher, 1982; Lipowsky 1982b, 1983, 1984a; Lipowsky and Speth, 1983; Kroll and Lipowsky, 1983b) for one-component systems in a semi-infinite geometry. For such systems, one has to consider *only two* thermodynamic fields such as temperature, T, and chemical potential, μ.

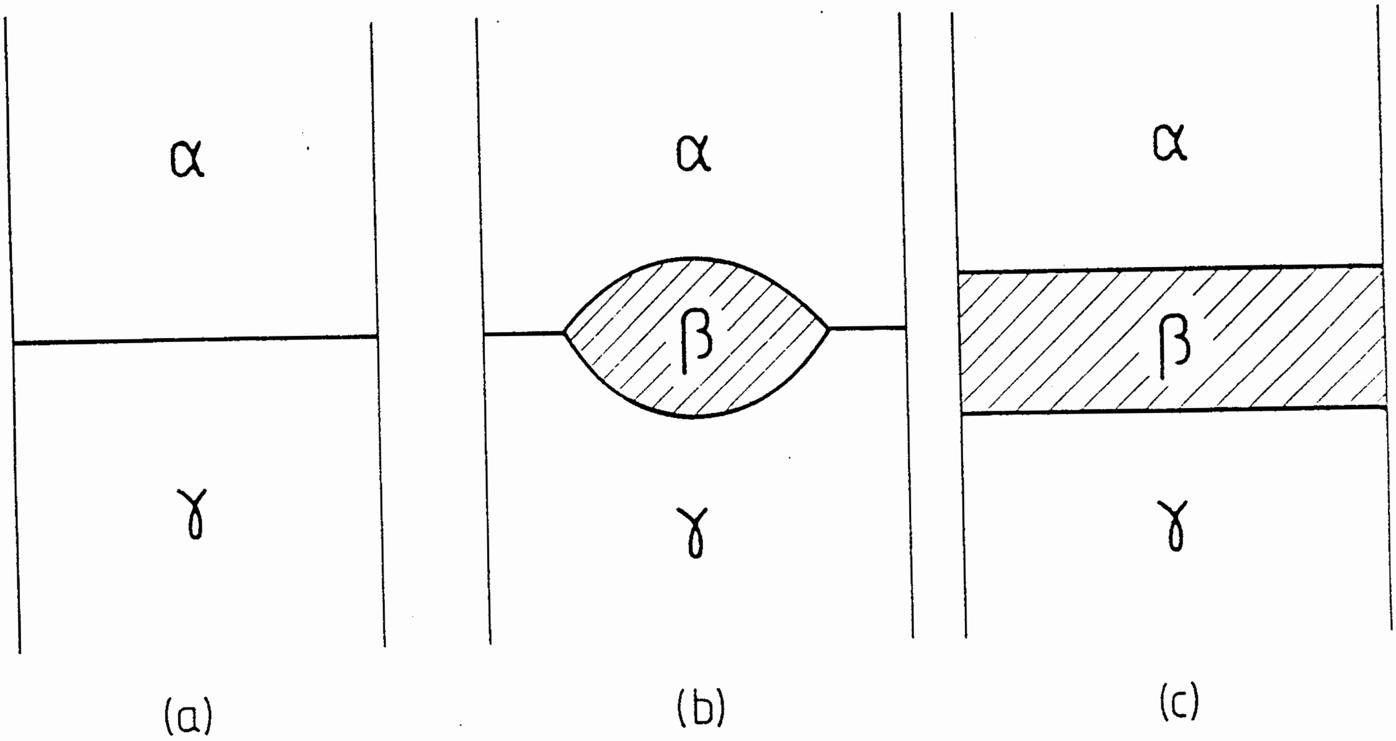

Fig.1: Close to $\alpha\beta\gamma$ coexistence, the $\alpha\gamma$ interface shown in (a) may contain droplets or a thin film of β phase. Droplets with a finite contact angle as in (b) correspond to incomplete wetting while a thin film as in (c) implies vanishing contact angle and complete wetting.

<table>
<tr><th></th><th>α</th><th>β</th><th>γ</th></tr>
<tr><td>Oil, water, and surfactant</td><td>oil-rich phase</td><td>micro-emulsion</td><td>water-rich phase</td></tr>
<tr><td>Binary mixture + vapor</td><td>vapor</td><td>liquid 1</td><td>liquid 2</td></tr>
<tr><td>Adatom gas + substrate</td><td>vapor</td><td>liquid or solid</td><td>solid(Sp)</td></tr>
<tr><td>Binary mixture + solid wall</td><td>liquid 1</td><td>liquid 2</td><td>solid(Sp)</td></tr>
<tr><td>Liquid crystal + solid wall</td><td>isotropic liquid</td><td>nematic liquid</td><td>solid(Sp)</td></tr>
<tr><td>Surface melting</td><td>vapor</td><td>melt</td><td>crystal</td></tr>
<tr><td rowspan="2">Binary alloy + surface</td><td>ordered</td><td>disordered</td><td rowspan="2">vapor(Sp)</td></tr>
<tr><td colspan="2">superlattice</td></tr>
<tr><td>Liquid crystal + surface</td><td>isotropic liquid</td><td>nematic/ smectic</td><td>vapor(Sp)</td></tr>
<tr><td>Binary alloy + domain wall</td><td>ordered 1</td><td>disordered</td><td>ordered 2</td></tr>
<tr><td>Grain boundary melting</td><td>crystal 1</td><td>melt</td><td>crystal 2</td></tr>
</table>

Table I : Physical systems for which complete or incomplete wetting of the $\alpha\gamma$ interface by the β phase has been observed. The spectator phase is denoted by (Sp). References are given in the text.

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