Wetting Transitions near Bulk Triple Points

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The effect of a bulk triple point between phases α, β, and γ on the wetting, by films of β or γ, of an $\alpha|\omega$ interface (between a wall ω and bulk α) is discussed phenomenologically. Various additional wetting and surface transitions are induced by the triple point and may be pinned by it, and a compound $(\beta\gamma)$ film may appear. The results are relevant to recent adsorption experiments and simulations.

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In this note we show that wetting transitions[1] on a substrate can be induced and pinned by a bulk triple point. This observation is relevant to recent experiments and simulations, and, although fairly straightforward, does not seem to have been stressed before.[2-4] For orientation, we first review normal wetting and prewetting transitions,[5a] then show how they can be driven by bulk triple points, and finally make a few remarks on experiments.[2-4] We shall use the language of adsorption from a vapor phase and thus plot phase diagrams in the (T,μ), or temperature and chemical potential, plane. However, the arguments apply equally to adsorption of a liquid or solid phase and to any type of triple point.

Consider two phases α (say, vapor) and β (say, liquid or solid) and a planar substrate or "wall," ω, which we regard as *inert*, but having a new relative attraction for phase β. Suppose, initially, that the system is *on*[6] the bulk first-order phase boundary along which α and β coexist: see bold lines in Fig. 1. If $\sigma_{\lambda\nu}\equiv\sigma_{\nu\lambda}$ denotes the surface tension of an interface, $\lambda|\nu$, between phases λ and ν, the inequalities

$$\delta\sigma_{\alpha\omega}{}^{\beta}\equiv\sigma_{\alpha\beta}+\sigma_{\beta\omega}-\sigma_{\alpha\omega}>0 \text{ and } \delta\sigma_{\beta\omega}{}^{\alpha}>0 \qquad (1)$$

imply that ω is not wetted by either α or β; i.e., the substrate is *nonwet* or *incompletely wet*,[5a] although there may be a *thin* adsorbed, β-like film of microscopic thickness l_β. On the other hand the equality $\delta\sigma_{\alpha\omega}{}^{\beta}=0$, or $\sigma_{\alpha\omega}=\sigma_{\alpha\beta}+\sigma_{\beta\omega}$, implies that a *macro*scopically thick ($l_\beta=\infty$) layer of β *completely wets*[5a] the interface $\alpha|\omega$, as indicated by the dots in Fig. 1. Now a surface wetting transition[5-7] in the α phase[6] occurs when, as T varies along a phase boundary,[6] the substrate goes from incompletely wetted by β to completely wetted by β. The transition may be continuous, with $l_\beta\to\infty$ at a *critical wetting point*,[5a,8] denoted $C_W{}^1$ [Fig. 1(a)], or it may be of first order, as at W in Fig. 1(b), where l_β jumps from a finite value.

In both cases one has a *thick* film, denoted (β), near the wet part of the phase boundary. In the latter case a first-order, $(\beta)\alpha$ *prewetting* boundary[5a] (across which l_β is discontinuous) emanates from W, moves away *tangentially* from the bulk $\alpha\beta$ phase boundary, and terminates at a prewetting critical point, $C_{\mathrm{pre}}{}^1$ in Fig. 1(b). If, as we will suppose, the (net) potential of attraction $V_{\beta\omega}(z)$ between β and ω decays with distance z as U_β/z^φ (where one expects $\varphi=3$),[5a,9] the tangency is described by $\Delta\mu_{\mathrm{pre}}\sim\Delta T^{\varphi^*}$ with $\varphi^*=\varphi/(\varphi-1)$; this behavior goes over to $\Delta T/\ln\Delta T$ when the bulk correlation length becomes large.[5b]

This scheme of surface transitions is anticipated if the interface $\alpha|\beta$ is *rough*. If it is *smooth*, wetting is expected to proceed via an unbounded

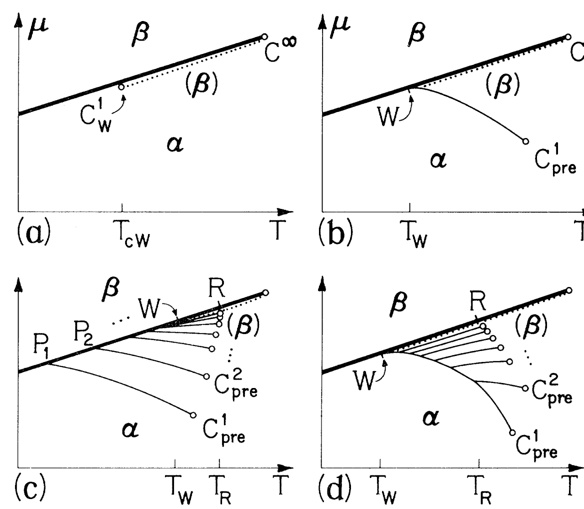

FIG. 1. Phase diagrams illustrating (a) critical wetting, (b) first-order wetting, and (c), (d), layering transitions and wetting (when $\alpha|\beta$ is smooth for $T<T_R$). The dots indicate wet regions of the bulk phase boundary; R denotes the roughening point.

sequence of *layering transitions* yielding a variety of phase diagrams, two of which are illustrated in Figs. 1(c) and 1(d). It is generally argued[5a,9] that $T_{c,n}$, the critical temperature at which the nth layering-transition boundary terminates, should approach T_R, the roughening temperature[9] of the $\alpha|\beta$ interface, when $n\to\infty$ (as in Fig. 1).

Now in Fig. 2 the bold lines represent *bulk* phase boundaries for a system with three bulk phases, α, β, and γ, which coexist at a *triple point* $T_{\alpha\beta\gamma}$. To study surface transitions in the phase α we compute and compare the free energies of possible adsorption structures, $\omega(\lambda\ldots)\alpha$, including the wall interactions and interfacial contributions. As customary in thermodynamics, the $\sigma_{\lambda\nu}$ and bulk free-energy densities are assumed to vary smoothly with T and μ and to extrapolate into "metastable" regions where, strictly, the phase structure in question might not exist. The physics is simply that the bulk phases, β and γ, may have markedly different substrate interactions so that, as T passes through $T_{\alpha\beta\gamma}$, new surface transitions are to be expected. There are four cases as follows:

(i) *No wetting.*—If one has $\delta\sigma_{\alpha\omega}{}^{\beta}>0$ and $\delta\sigma_{\alpha\omega}{}^{\gamma}>0$ the substrate is nonwetted both above and below $T_{\alpha\beta\gamma}$ and there is no wetting transition at the triple point. One may, however, anticipate a (possible weak) nonanalyticity in the $\alpha\omega$ surface free energy[7] at $T_{\alpha\beta\gamma}$, reflecting the bulk $\beta\gamma$ transition, as suggested by the solid dot in Fig. 2(a).

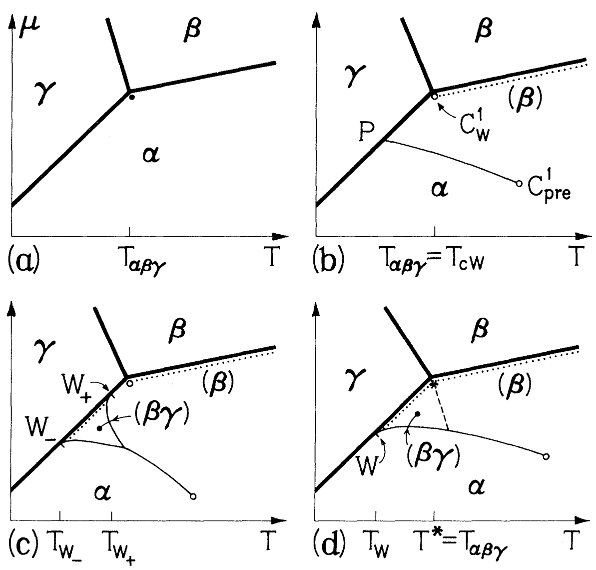

FIG. 2. Wetting and surface transitions near a bulk triple point, (a) when neither β nor γ wets the substrate, ω, and (b)–(d) when β wets $\alpha|\omega$ but γ does not.

(ii) *Wet-nonwet.*—When $\delta\sigma_{\alpha\omega}{}^{\beta}=0$ but $\delta\sigma_{\alpha\omega}{}^{\gamma}>0$ the substrate is completely wetted by β above $T_{\alpha\beta\gamma}$ but it is not wetted by γ below $T_{\alpha\beta\gamma}$. In the simplest situation, Fig. 2(b), a critical wetting point of new type appears precisely *at* the triple point with $l_\beta\to\infty$ as $T\to T_{\alpha\beta\gamma}{}^{-}$ along the $\alpha\gamma$ boundary. Note that a thick film, (β), persists some way *below* $T_{\alpha\beta\gamma}$ because the $\beta\omega$ attractions stabilize such a film *even when* the *bulk* β phase is *unstable* to *both* α *and* γ: thus "triple-point critical wetting arises" when the wetting of ω by β, that would have occurred on the $\alpha\beta$ boundary continued below $T_{\alpha\beta\gamma}$, is truncated by the intervening $\alpha\gamma$ boundary. The prewetting line shown in Fig. 2(b) is similarly truncated, at P, and, indeed, may be absent altogether.

There is no wetting in the immediate vicinity of this prewetting line. However, if $\delta\sigma_{\alpha\beta}{}^{\gamma}\equiv\sigma_{\alpha\gamma}+\sigma_{\beta\gamma}-\sigma_{\alpha\beta}$ is sufficiently small relative to[10] $D_\beta{}^{\alpha\omega}$, the strength with which β wets $\alpha|\omega$, a *compound film,* $(\beta\gamma)$, with structure $\omega(\beta\gamma)\alpha$, should be stabilized: l_β remains finite but $l_\gamma\to\infty$ at the $\alpha\gamma$ boundary. Thus wetting by γ is mediated by a thin β film even when γ cannot wet $\alpha|\omega$ directly! Then as in Fig. 2(c), both an ordinary, or lower, and an upper wetting transition appear near, but below, $T_{\alpha\beta\gamma}$ [with $T_{\alpha\beta\gamma}-T_{W-}$ varying as[10] $(\delta\sigma_{\alpha\beta}{}^{\gamma})^{\varphi^*}$]. Finally, if $\delta\sigma_{\alpha\beta}{}^{\gamma}=0$, so that γ wets $\alpha|\beta$ at the triple point, a line of continuous transitions (probably not actually singular in a full theory) emanates from a new wetting multicritical point at $T^*=T_{\alpha\beta\gamma}$ and separates the (β) and $(\beta\gamma)$ films as indicated in Fig. 2(d).

(iii) *Nonwet-wet.*—If γ wets $\alpha|\omega$ below $T_{\alpha\beta\gamma}$ but β does not wet $\alpha|\omega$ above $T_{\alpha\beta\gamma}$, we simply have the reverse of the previous case with the roles of β and γ interchanged.

(iv) *Wet-wet.*—When $\delta\sigma_{\alpha\omega}{}^{\beta}=\delta\sigma_{\alpha\omega}{}^{\gamma}=0$ the substrate may be wet both above and below $T_{\alpha\beta\gamma}$. If the phases β and γ are symmetrically related, with T replaced by, say, a magnetic field, one should obtain a diagram like Fig. 3(a) with a wetting transition pinned at the triple point; but the associated critcial point, $C_{\rm pre}{}^{1}$, may be replaced by a prewetting triple point with $(\gamma)\alpha$ and $(\beta)\alpha$ prewetting boundaries. In general, however, one phase, say β, will wet $\alpha|\omega$ more strongly, i.e., $\Delta_{\beta\gamma}\equiv D_\beta{}^{\alpha\omega}-D_\gamma{}^{\alpha\omega}>0$. Note that $\Delta_{\beta\gamma}$ measures the drop in the observed tension $\sigma_{\alpha\omega}(T)$ in passing through $T_{\alpha\beta\gamma}$ from the γ-wet to β-wet regions (although no actual discontinuity arises). Figure 3(b) illustrates the simplest situation: a critical β-wetting point occurs *at* the triple point, as in

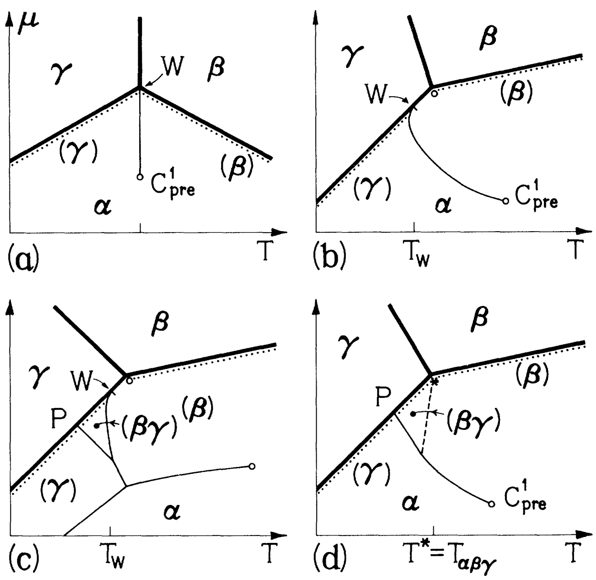

FIG. 3. Wetting transitions near a bulk triple point when both β and γ may wet ω: In (b)–(d) β wets more strongly.

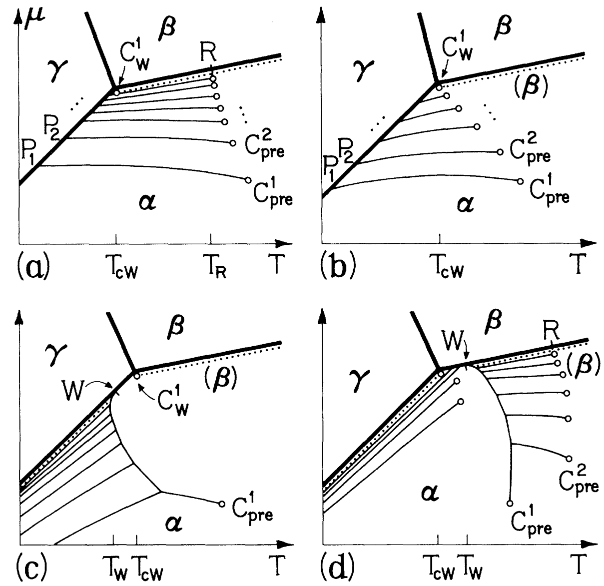

FIG. 4. Some possible multilayering phase diagrams for $\alpha|\omega$ smooth. In (a) and (b) β wets $\alpha|\omega$ but γ does not; in (c) β wets $\alpha|\omega$ more strongly than γ; vice versa in (d).

(ii), but an associated wetting transition, representing the $\gamma\beta$ transition *in* the adsorbed film, occurs below $T_{\alpha\beta\gamma}$ with $T_{\alpha\beta\gamma} - T_W \propto (\Delta_{\beta\gamma})^{\varphi^*}$. As in Fig. 3(c), the prewetting critical point may be replaced by a triple point and, if $\delta\sigma_{\alpha\beta}{}^{\gamma}/\Delta_{\beta\gamma}$ is small enough,[10] W moves closer to the triple point and a compound film $(\beta\gamma)$ again appears. The new prewetting line $(\gamma)(\beta\gamma)$ is, for small $\Delta_{\beta\gamma}$, parallel to the bulk $\gamma\beta$ boundary. Lastly, again as in (ii), if γ wets $\alpha|\beta$ ($\delta\sigma_{\alpha\beta}{}^{\gamma} \equiv 0$), a critical line emanates from a wetting multicritical point *at* the triple point as in Fig. 3(d) [where, once more, $(\beta)\alpha$ and $(\gamma)\alpha$ prewetting lines may appear].

The triple-point-driven phase diagrams displayed in Figs. 2 and 3 apply only if the interfaces $\alpha|\beta$ and $\alpha|\gamma$ are rough. As in Fig. 1, smooth interfaces should lead to *layering transitions*.[9] Thus if both interfaces are smooth (below some T_R) the wet-nonwet case, (ii), can give rise to Fig. 4(a). On the other hand, if $\alpha|\gamma$ is smooth but $\alpha|\beta$ rough, $T_{\alpha\beta\gamma}$ acts as a roughening temperature for γ layering transitions; see Fig. 4(b). In the same circumstances ($\alpha|\beta$ rough, $\alpha|\gamma$ smooth) the wet-wet case, (iv), can yield a diagram like Fig. 4(c) in which β wets ω preferentially (i.e., $\Delta_{\beta\gamma} > 0$). Conversely, Fig. 4(d) represents a possible phase diagram in the wet-wet case with $\Delta_{\beta\gamma} < 0$ and both interfaces smooth.

Many other possibilities for layering transitions exist and may well occur.[5a]

Most current experiments on multilayer adsorption[2,3] have been performed on systems where α is a fluid phase (usually a gas), β liquid or solid, and γ a solid phase. We believe that the schematic phase diagrams we have presented here should be relevant to these and other experiments. Indeed, ethylene on graphite[3] may well have a phase diagram similar to that in Fig. 4(b). Likewise the study by Awschalom, Lewis, and Gregory[2] of oxygen on graphite has provided some evidence for a phase diagram like Fig. 4(d) in the vicinity of the β-oxygen (our γ), γ-oxygen (our β), and gas triple point. The two crystalline phases differ strongly in their magnetic properties so that marked changes in substrate interactions are expected. Finally, Ebner[4] has recently simulated wetting in a six-state Potts model, finding phase diagrams like Fig. 4(c), although with the extra feature that T_R may fall below T_W so that high-order layering critical points appear before the $(\gamma)(\beta)$ boundary is reached.

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