Incomplete wetting by adsorbed solid films

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The free energy of an adsorbed solid film is examined on a phenomenological basis, taking into account the elastic energy as well as substrate-adsorbate interactions. The equilibrium film is found generally to be strained relative to the bulk lattice spacing along directions parallel to the adsorption plane. The resulting equilibrium film thickness does not diverge at the bulk solid phase boundary except possibly at special points. The data for noble gases on graphite are reviewed from this point of view.

The equilibrium thickness of adsorbed films has been a topic of recent experimental[1,2] and theoretical interest.[3-5] A crystalline film of finite thickness may coexist with a stable bulk liquid or gas phase. As the bulk fluid-to-solid phase transition is approached, the thickness of this film may or may not diverge. These two possibilities are termed *complete* and *incomplete* wetting at coexistence, respectively.[1,3] It was originally suggested that complete wetting should occur quite generally for sufficiently attractive substrates.[3] However, recent experimental work has not found this to be the case,[1] and it has been suggested that "mismatch" in crystal structure or lattice constants between the film and the bulk solid may play an important role in determining equilibrium film thickness.[1,6] The phenomenological accounting of film free energy undertaken below confirms this suggestion. In fact, it appears that complete wetting by an adsorbed crystalline film should only occur in special cases where the net stress tending to strain the film parallel to the substrate vanishes. However, if this stress is small then the film thickness at bulk coexistence will be large and the fact that it is finite may be difficult to detect. Crystalline adsorbed films exhibiting complete or near complete wetting should therefore be only weakly strained, like Kr (Refs. 1 and 7) or Ar (Refs. 1 and 8) on graphite. On the other hand, films on relatively attractive substrates that exhibit incomplete wetting should be more strained, like Ne (Refs. 1 and 9) on graphite, or have crystal structure different from the bulk, like O_2 (Refs. 1 and 10) on graphite. Further study of the relationship of wetting behavior to mismatch between bulk and film lattices appears to be called for.

Let us consider a crystalline film of n layers adsorbed on an attractive substrate and in equilibrium with a bulk fluid (liquid or gas) phase at given temperature and pressure on the bulk fluid-solid coexistence curve. Let us assume, for simplicity, that the lattice structure of the film is identical to that of the bulk solid. The stresses at the substrate-film interface and at the film's free surface will strain the film by an amount ϵ parallel to the plane of adsorption. This strain results in a mismatch between film and bulk solid lattice constants and therefore generally hinders growth of the film into an arbitrarily thick layer, as is argued below. If the adatom-substrate potential, $\phi(z)$, is very strongly attractive near the substrate (small z) then the equilibrium film may have dislocations in its first few layers, as is discussed in more detail at the end of this paper. However, these dislocations will be confined to the interfacial region and so may be considered part of the substrate-film interface. The strain ϵ is that of the remaining layers above any such substrate-induced dislocations. At long distances from the

substrate the van der Waals attractions are assumed to dominate in the adatom-substrate potential[3] so that $\phi(z) \sim z^{-3}$. (The crossover to z^{-4} behavior at very long distances does not change any of the conclusions reached below and will be ignored here.)

The free energy of this adsorbed film of n layers and parallel strain ϵ may be divided into four parts. First, there is the elastic energy per unit area,

$$F_{el}(n, \epsilon) = \tfrac{1}{2} nK\epsilon^2 + O(n\epsilon^3) \ , \tag{1}$$

due to the strain in the entire film. Second and third are the surface energies per unit area, $\Sigma_1(\epsilon)$ and $\Sigma_2(\epsilon)$, of the substrate-film and film-fluid interfaces, respectively. The elastic constant K in (1) and Σ_1 and Σ_2 are evaluated in the limit $n \to \infty$, so have *no* dependence on n. Thus the fourth term in the film's free energy is simply all the remaining finite-thickness effects that are not included in the first three terms. For large thicknesses, n, the leading finite-thickness correction should be due to the long-range (van der Waals) substrate-adatom potential[3-5] and falls off as n^{-2}. If we expand the surface energies about zero strain[11] as

$$\Sigma_i(\epsilon) = \Sigma_i + \epsilon\Sigma_i' + O(\epsilon^2) \ , \tag{2}$$

the full free energy of the film is then

$$F(n, \epsilon) = \tfrac{1}{2} nK\epsilon^2 + \Sigma_1 + \epsilon\Sigma_1' + \Sigma_2 + \epsilon\Sigma_2' + O(n\epsilon^3, \epsilon^2, n^{-2}) \ . \tag{3}$$

The equilibrium film thickness and strain is obtained by minimizing (3); it is instructive to do this in two stages. For a given film thickness, n, the equilibrium strain is

$$\epsilon_n = -\frac{\Sigma_1' + \Sigma_2'}{nK} + O(n^{-2}) \ . \tag{4}$$

The resulting free energy as a function of film thickness at equilibrium strain is then

$$F_n \equiv F(n, \epsilon_n) = \Sigma_1 + \Sigma_2 - \frac{1}{2}\frac{(\Sigma_1' + \Sigma_2')^2}{nK} + O(n^{-2}) \ . \tag{5}$$

The equilibrium film thickness n_0, which is obtained by minimizing F_n, will clearly be finite except possibly when $\Sigma_1' + \Sigma_2' = 0$. Thus *complete* wetting by an adsorbed solid film will only occur at special points on the coexistence curve for which the parallel stress on the film ($\Sigma_1' + \Sigma_2'$) vanishes and then only if the term of order n^{-2} in (5) is positive. The actual value of n_0 depends on the long-range part of the

substrate-adsorbate potential and on the higher-order terms neglected in (1) and (2), but should generally behave as

$$n_0 \sim \frac{K}{(\Sigma_1' + \Sigma_2')^2} \qquad (6)$$

near a point of complete wetting. The equilibrium thickness at bulk coexistence, n_0, will thus be large or divergent for films that are only slightly strained, and consequently have only a small elastic contribution to their total free energy. On the other hand, for films that are more strained the elastic energy will be important and the equilibrium film thickness will not be large, giving incomplete wetting.

Most of the available data for noble gases on graphite is consistent with this general rule, although more study of wetting behavior and film lattice structure is needed before any firm conclusions can be drawn. Seguin and co-workers[1] have found that Ne exhibits incomplete wetting, while Ar, Kr and Xe show complete wetting, at least up to approximately ten layers. Calisti, Suzanne, and Venables[9] have found that at 14.7 K the monolayer of Ne on graphite has lattice spacing 3.15 Å at vapor pressure of 1.1×10^{-6} Torr, 3.09 Å at 5.7×10^{-5} Torr, while the bulk solid which will not form until about 10^{-1} Torr has a lattice spacing of 3.17 Å.[12] Thus the Ne film, which shows incomplete wetting at 7–8 K (Ref. 1) is strained by 3% or more in the monolayer regime at 14.7 K. In contrast to these results for Ne, Shaw and Fain[8] found that the lattice spacing in Ar films at around 30 K is essentially constant at the bulk value of 3.77 Å as bulk coexistence is approached from the monolayer regime at less than half the pressure. Ar films exhibit apparently complete wetting at 10–20 K.[1] Similarly, Fain and Chinn[7] have found that the lattice spacing of a bilayer of Kr on graphite is 4.02 ± 0.02 Å at 47 K and 4×10^{-6} Torr, which matches the bulk lattice spacing of 4.02 Å at the same temperature and solid-vapor coexistence (approximately 2×10^{-5} Torr).[7,12] This weakly strained Kr film on graphite shows apparently complete wetting at 15–50 K.[1]

The data for Xe on graphite do not fit as neatly as those for Ne, Ar, and Kr. Hammonds et al.,[13] have measured the lattice spacing of the Xe film at 112 K, which decreases from 4.45 Å in the compressed monolayer to 4.42 Å in the bilayer, as compared with 4.43 Å for bulk Xe at coexistence and that temperature.[12] This suggests that the Xe film is only slightly strained and should exhibit complete or almost complete wetting, consistent with the observations of Seguin et al.[1] for 10–60 K. However, Schabes-Retchkiman and Venables[14] have found that at approximately 60 K the compressed monolayer is actually commensurate with the graphite, thus having lattice spacing 4.26 Å, well below the bulk lattice spacing of 4.37 Å at that temperature.[12] They did not report the lattice constant of the bilayer; perhaps the relatively large strain is peculiar to the monolayer, which can thereby be commensurate with the substrate. Further measurements of the lattice spacings in the multilayer regimes of this and other solid films appear to be called for.

One possible limitation of the above phenomenological treatment of the solid film's free energy is that it ignores fluctuation effects. The fluctuations in the upper, film-fluid interface certainly play an important role in some models of wetting transitions (see, e.g., Ref. 4). The contribution of these fluctuations in the thick film ($n \to \infty$) limit is contained in the surface energy $\Sigma_2(\epsilon)$, so that it is only the limitation of these fluctuations due to finite film thickness that has been ignored. However, this reduction of surface entropy falls off with film thickness more rapidly[15] than the elastic energy, thus cannot change the conclusions reached above.

Let us now return to the question of when and where there will be dislocations in equilibrium adsorbed solid films. The parallel stress on a thick film that is causing the strain (4) is due to, and thus exerted at or near, the two interfaces bounding the film. The film will be stable against the introduction of dislocations as long as these stresses do not exceed a threshold proportional to the energy per unit length of a dislocation. The stress, Σ_2', at the upper, free surface of the film which works to dilate the film will almost certainly not exceed this threshold. The stress, Σ_1', at the substrate-film interface arises from the substrate attraction, $\phi(z)$, which couples to the local particle density, working to compress the film and giving a stress field that falls off at long distances as $\sigma(z) \sim z^{-3}$. If the attraction, and thus the stress Σ_1', do not exceed the threshold for dislocation production, then the equilibrium film will be dislocation free and the simple expression (1) for the elastic energy follows. In particular, films that exhibit complete or near complete wetting due to being weakly stressed should be dislocation free.

Once the substrate-adatom attraction exceeds the threshold, dislocations are introduced into the film. Let us first consider the case of a very small density of dislocations so that the interactions between the dislocations may be ignored. The stress field due to the substrate, $\sigma(z)$, produces a force on each dislocation, repelling it from the substrate. However, the energy of the dislocation's stress field diverges as the logarithm of the substrate-dislocation distance and this results in a force, proportional to z^{-1} at long distances, attracting the dislocation to the substrate.[16] The resulting equilibrium dislocation position is some finite number of layers from the substrate (probably one layer in many cases), even in the thick film limit. Thus it is consistent to consider these substrate-induced dislocations to be part of the substrate-film interface.

For very strongly attractive substrates the density of dislocations will be such that the typical spacing between dislocations near the substrate is comparable with that between substrate and dislocations, and the repulsive interaction between dislocations will play a role in determining the equilibrium dislocation positions. This will presumably result in some dislocations being pushed further into the film than others. Precisely, what the resulting equilibrium distribution of dislocation looks like is not obvious. However, the effective force on a dislocation attracting it to the substrate and falling off as z^{-1} at long distances will still be present and this should limit the depth of penetration of the dislocations for any finite substrate strength.

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